A NEW SEMIEMPIRICAL METHOD FOR ELECTRONIC STRUCTURE

By

YA-WEN HSIAO

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To my dear
father,
little sister, Jing-Wen,
husband, Magnus,
and to the memory of my dear mother

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By

Ya-Wen Hsiao

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Chairman: Michael C. Zerner
Major Department: Chemistry

A modified semiempirical molecular orbital method, XINDO, is developed at the INDO level. The commonly applied Goeppert-Mayer-Sklar approximation is no longer included, and a short range repulsive term, the effective core potential, is introduced to compensate the penetration effect which causes errors in calculating molecular geometries. The XINDO Hamiltonian is constructed over the Slater type functions. During each SCF cycle, we solve the secular equation with non-identity overlap matrix. In this way, we incorporate the overlap into the XINDO method. This improves on the geometry calculations, and the energy description of antibonding molecular orbitals. Multi-center terms are also added by both modifying the off-diagonal part of the STO Hamiltonian representation, and indirectly through the SCF procedure.

The XINDO model has been implemented for H, C, N, and O which are the main constituents of most of the organic molecules. The model can be applied to calculate electronic excitations and molecular geometries by using the semiempirical two-electron integrals which are conventionally used only for calculating spectra. The results of the calculated geometries are quite satisfactory, and the calculated charge distributions and inter-atomic angles are improved through the inclusion of multi-center integrals.

CHAPTER 1
INTRODUCTION

After several decades, the development of electronic structure computational techniques has become quite mature. *Ab initio* methods provide accurate results for smaller molecular systems, especially for ground state properties. However, when it comes to systems of biological or pharmacological significance, *ab initio* treatment becomes prohibitive due to the computational demands that arise from the increase in the number of electrons. Moreover, a reasonable description of the excited states of molecules is still difficult to achieve. However, it is possible today to use *ab initio* methods to do expensive calculations to obtain approximate excited state descriptions for small-sized molecules. Nevertheless, *ab initio* methods are still not applicable in practical studies involving large systems. For example, the study of the primary electron transfer mechanism of bacterial photosynthesis is an active subject. The electron moves from the special pair to a bacteriopheophytin-b within 3 ps and hence makes experimental investigations difficult. Since the entire protein complex consists of more than 10,000 heavy atoms, it is impractical to use *ab initio* quantum mechanics for theoretical predictions.

Semiempirical electronic structure methods, on the other hand, offer an alternative way of treating the electronic structures of large systems using quantum mechanics. Most of the large proteins or complex compounds consist of smaller-sized functional groups in which individual molecular properties are conserved. Based on these smaller organic molecules many semiempirical methods are parameterized to fit the experimental data of the these properties. This offers an advantage to semiempirical methods in that they are able to describe all classes of molecules averagely well for general purposes. The disadvantage of using the semiempirical methods is that calculations of electronic spectra are not available in most of the methods, and the methods which are able to calculate spectra cannot in general be used to calculate molecular geometry. Therefore, the few methods for calculating electronic excitations do not give meaningful ground state potential energy surfaces, not to mention excited states potential energy surfaces.

The motivation of this thesis is to find a semiempirical method which can yield reasonable molecular geometries as well as electronic spectra.

There may arise two questions to this motivation. First of all, why do we choose semiempirical methods? Because we want to have a method which can help in our studies on big molecular systems, and as it has been stated previously, *ab initio* methods are still restricted to smaller molecules. The second question is: why do we bother to have a method which is multi-purposed? The most straightforward answer is that such a method is more convenient for users to use for calculations of all properties, instead of changing from method to method only because the range of applicability of each methods is limited. Another advantage is that the calculated properties are consistent. The ground state potential energy surface obtained from such method will be correct within the accuracy of the method, and the electronic excitations will also be good. Then the next possible step is to create the excited state potential energy surface based on the ground state potential surface and the electronic excitations. With such a method one may imagine that it becomes possible to study the excited states of a system as, e.g., the photosynthesis reaction center mentioned previously.

Yet, there are other problems existing in semiempirical methods, such as the difficulty in obtaining correct conformational structures, rotational barriers, binding energies, etc.. This makes the semiempirical methods open to further improvement. Hence we will attempt to design the new method to improve these shortcomings as they become known.

Many assumptions have been made for semiempirical methods in order for them to yield fast and correct answers with low cost. In the new method, however, we will bring back more of the physics that has been omitted in earlier semiempirical methods. More integrals may need to be added, but this must be done with great care so that we will not destroy the advantage of the semiempirical methods. We first review the most commonly used semiempirical methods: the ZDO (zero differential overlap) type methods and the EHT (extended Hückel theory). Especially the assumptions behind the methods need to be understood and the invalidity re-examined. Second, we will learn from the existing models and combine the useful parts of them into the new model.

In summary, we think that we have adopted the strong points of both the EHT method (the inclusion of the overlap) and the ZDO methods (systematically reducing the number of two-electron integrals) in the design of XINDO. The molecular geometries obtained by using the XINDO method are quite satisfactory. The choice of the two-electron integrals promises the applicability of the electronic excitation calculations. The new method, XINDO, is indeed full of potential.

CHAPTER 2
THEORY REVIEW

2.1 The Molecular Problem

2.1.1 Time-independent Schrödinger Equation

Solving the time-independent Schrödinger equation [1]

$$H\Psi_I = E_I\Psi_I \tag{2.1}$$

offers a way to obtain properties of chemical substances. In the Schrödinger equation, H is the Hamiltonian operator, E_I is the total energy of the state I of the system, and Ψ_I is the wavefunction describing the stationary states of the system, e.g., a molecule. The usual time-independent Hamiltonian operator for a molecular system consisting of N electrons and M atoms is

$$\begin{aligned} H &= -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \sum_{A=1}^{M}\frac{\hbar^2}{2M_A}\nabla_A^2 - \sum_{A=1}^{M}\sum_{i=1}^{N}\frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \sum_{A=1}^{M-1}\sum_{B=A+1}^{M}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R_{AB}} \\ &+ \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{e^2}{4\pi\epsilon_0 r_{ij}}, \end{aligned} \tag{2.2}$$

where the first two sums are the kinetic energy operators of electrons and nuclei, respectively, the third sum is the attraction between electrons and nuclei, and the last two sums are the electron-electron and nuclear-nuclear repulsions, respectively. Other interactions such as spin-orbit coupling can be added, depending on the purpose of the calculation.

2.1.2 Born-Oppenheimer Approximation

Except for the nuclear-electron attraction term in Eqn. (2.2), other electronic and nuclear terms are independent of each other. It seems possible to simplify the process of solving the Schrödinger equation by separating the electronic and nuclear motions, i.e., the Born-Oppenheimer [2] approximation. This approximation is based on the fact that the nuclear mass is at least 1836 times the mass of an electron, hence the electrons move much faster than the nuclei. One may therefore assume that electrons move in a field generated by a frozen nuclear configuration. The approximate molecular wavefunction is written as a product of an electronic part and a nuclear part

$$\Psi(x, X) = \psi_{el}(x; X)\psi_{nucl}(X), \tag{2.3}$$

where x indicates the electronic coordinates and X is the nuclear coordinates. The notation $\psi_{el}(x; X)$ indicates that the nuclear coordinates enters the electronic wavefunction only parametrically. For a given nuclear configuration, X, the electronic wavefunction may then be obtained from solving the electronic part of the Schrödinger equation.

$$H_{el}(x; X)\psi_{el}(x; X) = E_{el}(X)\psi_{el}(x; X). \tag{2.4}$$

$E_{el}(X)$ together with the nuclear repulsion energy, which is a constant for each set of X and can therefore be added after Eqn. (2.4) is solved, serve as a potential energy $V_{nucl}(X)$ in which the nuclei move [2, 3]. The global minimum of $V_{nucl}(X)$ occurs at the most stable nuclear configuration, i.e., at the equilibrium.

2.1.3 Variational Principle

Consider a system described by a Hamiltonian H and with a normalized ground state wavefunction Ψ_0. Then the energy expectation value of the Hamiltonian with respect to any normalized trial wavefunction Φ, is always greater or equal to the true ground state energy of the system:

$$E(\Phi) = \langle\Phi|H|\Phi\rangle \geq E_0. \tag{2.5}$$

The energy $E(\Phi)$ is a functional of the Φ's, and fully minimizing $E(\Phi)$ with respect to variations in the trial wavefunctions gives the true ground state Ψ_0, and the energy $E(\Psi_0) = E_0$, which is indicated in Eqn. (2.5) where the equality holds when Φ is identical to Ψ_0.

Since the Schrödinger equation cannot be solved exactly, except for the simplest cases, we are more interested in finding approximate solutions. One way is to apply the variational principle, since one may always find an upper bound to E_0 according to Eqn. (2.5).

2.1.4 The Hartree-Fock Method for Molecules

Due to the cumbersome electron-electron interaction term, the only systems of electrons and nuclei that can be exactly solved are the hydrogen atom and systems such as H_2^+ within the Born-Oppenheimer approximation because there is only one electron. For many-electron systems, since the inter-electronic repulsion term in the Schrödinger equation is not separable, further approximation is needed. One can obtain the zeroth order wavefunction of any many-electron system by neglecting the inter-electronic repulsions, and then the solution to the resulting Schrödinger equation can be expressed as a product of many one-electron functions:

$$\Psi^{(0)}(x_1, x_2, \cdots, x_N) = \psi_1(\mathbf{r}_1 : s_1)\psi_2(\mathbf{r}_2 : s_2)\cdots\psi_N(\mathbf{r}_N : s_N), \tag{2.6}$$

where x_i contains the spatial ($\mathbf{r}_i$) and spin (s_i) descriptions of the ith electron, i.e., $x_i = (\mathbf{r}_i : s_i)$. The procedure of calculating these one-electron functions was introduced by Hartree [4]. In the Hartree theory the product wavefunction Eqn. (2.6) is used as a variational many-electron wavefunction in Eqn. (2.5). This results in a Schrödinger like equation for each ψ_i where the cumbersome electron-electron interaction is replaced by an average interaction (same as Eqn. (2.14)).

From now on we will proceed our discussion using atomic units in which $\hbar$, $e^2/4\pi\varepsilon_0$ and m_e are all equal to one.

However, since the true many-electron Schrödinger equation is not separable, the true wavefunction can not be expressed exactly as a product of many one-electron functions and, moreover, Eqn. (2.6) does not satisfy the Pauli exclusion principle

[5], which states that a many-fermion wavefunction has to change sign under the interchange of two particles,

$$\Psi(x_1, \cdots, x_i, \cdots, x_j, \cdots, x_N) = -\Psi(x_1, \cdots, x_j, \cdots, x_i, \cdots, x_N). \tag{2.7}$$

The state of an electron is not determined from the spatial orbital only but one also has to consider its spin state. Keeping the single particle approximation, the approximate many-electron wavefunction must be written as an antisymmetric linear combination of product wavefunctions using spin orbitals. This was pointed out by Fock [6] and Slater [7]. An SCF calculation that uses antisymmetrized spin orbitals is called a Hartree-Fock (HF) calculation. A convenient way of representing the antisymmetric linear combination of the Hartree SCF wave function, is the Slater determinant [8]

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_N(2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(N) & \psi_2(N) & \cdots & \psi_N(N) \end{vmatrix} = \frac{1}{\sqrt{N!}} \sum_{\mathcal{P}} (-1)^p \mathcal{P} \psi, \tag{2.8}$$

where $\mathcal{P}$ are the permutation operators of the symmetric group of order N.

With the assumption that the Slater determinant Eqn. (2.8) is an approximation to the ground state many-electron wavefunction, one may use the variational principle

Eqn. (2.5) to minimize the energy given by

$$\begin{aligned} E_0 &= \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{i,j}\langle ij||ij\rangle \\ &= \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{i,j}(\langle ij|ij\rangle - \langle ij|ji\rangle), \end{aligned} \tag{2.9}$$

where the one electron operator h is given by

$$h(1) = -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}}, \tag{2.10}$$

and the two-electron integrals are given by

$$\langle ij|kl\rangle = \int dx_1 dx_2 \psi_i^*(1)\psi_j^*(2) r_{12}^{-1}\psi_k(1)\psi_l(2). \tag{2.11}$$

Such a procedure leads to a Schrödinger-like equation for the one-electron wave functions, the Hartree-Fock equation:

$$f\psi_i = \varepsilon_i \psi_i, \tag{2.12}$$

where the Fock-operator is given by

$$\begin{aligned} f(1) &= h(1) + \sum_j^{occ}(J_j(1) - K_j(1)) \\ &= h(1) + \sum_j^{occ}\int dx_2 \psi_j^*(2) r_{12}^{-1}(1 - \mathcal{P}_{12})\psi_j(2). \end{aligned} \tag{2.13}$$

The operator $\mathcal{P}_{12}$ interchange electron 1 and 2, and J_j is the Coulomb operator, which represents the average Coulomb interaction between the electrons. K_j is the exchange operator, which comes from the requirement of an anti-symmetric wavefunction; that is,

Coulomb operator:

$$J_j\psi_i(1) = \int dx_2\psi_j^*(2)r_{12}^{-1}\psi_i(1)\psi_j(2), \tag{2.14}$$

Exchange operator:

$$K_j\psi_i(1) = \int dx_2\psi_j^*(2)\psi_i(2)r_{12}^{-1}\psi_j(1) \tag{2.15}$$

From Eqn. (2.13) it is clear that the Fock operator depends on the wavefunction through the Coulomb and exchange operators. Therefore the Hartree-Fock equation is not linear and is generally solved iteratively.

A particular way of solving the HF equation is to write each molecular orbital as a linear combination of atomic orbitals (LCAO-MO) [9, 10]. Let $\{\phi_1, \cdots, \phi_\mu, \cdots, \phi_K\}$ denote a set of K real atomic orbital functions to build up our trial ith molecular orbital function ψ_i

$$\psi_i = \sum_{\mu=1}^{K} \phi_\mu c_{\mu i}, \tag{2.16}$$

where $c_{\mu i}$'s are the expansion coefficients to be determined. Solving the Hartree-Fock equation Eqn. (2.12) with this trial wavefunction, one obtains

$$f(1)\psi_i(1) = f(1)\sum_{\mu=1}^{K}\phi_\mu(1)c_{\mu i} = \varepsilon_i \sum_{\mu=1}^{K}\phi_\mu(1)c_{\mu i}. \tag{2.17}$$

Multiplying Eqn. (2.17) from the left by ϕ_ν^* and integrate, one arrives at the secular equation, often called Roothaan equation,

$$\mathbf{Fc} = \mathbf{\Delta cE}, \tag{2.18}$$

where $\mathbf{E}$ is a diagonal matrix with the energy eigenvalues on the diagonal and $\mathbf{\Delta} \equiv \mathbf{1} + \mathbf{S}$. The matrices $\mathbf{S}$ and $\mathbf{F}$ are defined through

$$S_{\mu\nu} = \langle \phi_\mu(1)|\phi_\nu(1)\rangle, \text{ for } \mu \neq \nu, \tag{2.19}$$

$$F_{\mu\nu} = \langle \phi_\mu(1)|f(1)|\phi_\nu(1)\rangle. \tag{2.20}$$

From Eqn. (2.18) we get K eigenfunctions, $\psi_1, \cdots, \psi_i, \cdots, \psi_K$, with the corresponding energy eigenvalue ε_i:

$$\varepsilon_i = \langle i|h|i\rangle + \sum_j^{occ}\langle ij||ij\rangle. \tag{2.21}$$

In the case of closed-shell N-electron system, $N/2$ spatial eigenfunctions are occupied.

The approximate electron energy E_{el},

$$E_{el} = \sum_{i}^{N} \varepsilon_i - \frac{1}{2} \sum_{i,j}^{occ} \langle ij || ij \rangle, \tag{2.22}$$

is the upper bound of the true ground state energy, according to the variational principle. The energy is not equal to the sum of eigenvalues, since in that case the two-electron interaction would be counted twice. As was mentioned above, the Fock equation depends on the trial functions, and is generally solved by an iterative process. This is called the self-consistent-field method. The criteria for deciding when to stop the iteration is most commonly given by the difference of the density matrices of the current cycle and the previous one. The definition of the density matrix elements is

$$P_{\mu\nu} = \sum_{i}^{K} n_i c_{\mu i} c_{\nu i}^{*}, \tag{2.23}$$

where n_i is the occupation number of molecular orbital i. If the density matrix is equal to the result from the previous iteration within a given tolerance, then the electrostatic field is said to be self-consistent.

2.1.5 Koopmans' Theorem

In the previous section it was shown that adding up the HF orbital energies ε_i does not give the total energy, since in that case the Coulomb and exchange energies would be counted twice. What physical meaning can be given to the HF orbital energies?

Consider an N-electron system with a ground state Slater determinant ${}^{N}\Psi_0$, built from the N-HF orbitals ψ_i with the lowest energies. Take this N-electron system and compare to the systems where an electron is either added or removed, but keeping the set of orbitals $\psi_1, \cdots, \psi_k$ obtained from the HF calculation on the N-electron system. The energy expectation values are

$$\begin{aligned} {}^{N}E_0 &= \langle {}^{N}\Psi_0 | H | {}^{N}\Psi_0 \rangle, && (2.24) \\ {}^{N-1}E_i &= \langle {}^{N-1}\Psi_i | H | {}^{N-1}\Psi_i \rangle, && (2.25) \\ {}^{N+1}E^a &= \langle {}^{N+1}\Psi^a | H | {}^{N+1}\Psi^a \rangle, && (2.26) \end{aligned}$$

where the subscript i denotes that an electron has been removed from occupied orbital ψ_i and the superscript a means that an electron is added to a virtual orbital ψ_a. The ionization potential in this frozen orbital frame:

$$ {}^{N-1}E_i - {}^{N}E_0 = -\varepsilon_i, \tag{2.27}$$

and similarly,

$$ {}^{N}E_0 - {}^{N+1}E^a = -\varepsilon_a, \tag{2.28}$$

is the electron affinity.

However, Koopmans' theorem tends to give too positive ionization potentials and too negative electron affinities. Yet, Koopmans' approximation is still reasonable for the ionization potential for a neutral species or a positive ion for delocalized molecular orbitals, although it is not ideal for the electron affinity of a neutral or a negative species. There are two error sources when applying Koopmans' theorem. The first is that the orbitals of the ionic system are assumed to be the same as the orbitals of the neutral system; i.e., the orbitals are frozen. The energy for the ion calculated with these orbitals is higher than it would be if one would allow for the orbitals to relax. The other source of error is the lack of correlation in the HF procedure. One would expect the correlation correction to be larger for the state with the larger number of electrons. Since the correlation energy is a negative quantity one may assume that the neglect of electron correlation somewhat cancel the error from the frozen orbitals in the case of ionization potentials but adds to the error in the estimate of the electron affinities.

2.1.6 Electron Correlation

A Hartree-Fock SCF wave function describes the interactions among electrons in an average way as shown in Eqn. (2.14) . The error in the energies from HF calculations is of the magnitude of 1% which can be very dramatic for certain properties, such as bonding energies.

The difference between the exact energy for a specified non-relativistic Hamiltonian and the HF energy for the same system is defined as the correlation energy [11].

What is the nature of the correlation energy? An electron in, e.g., a molecule feels the actual Coulomb repulsion from the other electrons and therefore tend to avoid each other more than what is the case when using the average Coulomb potential Eqn. (2.14). In other words the electron motion is correlated and this gives rise to a lowering of the energy. This is normally referred as the "dynamic correlation" and it usually represents the largest part of the total correlation energy. The other source of the electron correlation is the so-called "essential correlation." It arises when one attempts to describe the electronic structures with a single Slater determinant.

Solving the full Schrödinger equation with the actual electron repulsion is impossible for a system with many electrons. However, there are other ways to at least partially calculate the correlation energy and thus correct the HF results. Two such methods are configuration interaction (CI), and many-body perturbation theory.

2.2 Semiempirical Methods

Despite the lack of electron correlation, the HF SCF method is quite accurate in describing molecular properties. However, the evaluation of integrals has made the method limited to smaller molecules and highly demanding of computer resources. The cost of calculation increases as the number of electrons increases. Given K basis functions then the evaluation of two-electron integrals is formally an K^4 process, and, in order to get better description of the system, large basis sets are needed. In order to shed some light of large systems like proteins, organo-metalic complex compounds, alternative ways must be sought.

Consider the molecular Hamiltonian expressed in second quantization formalism in an orthonormal molecular basis $\{\psi_p\}$ [12]:

$$H = \sum_{p,q} h_{pq} a_p^+ a_q + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle a_p^+ a_q^+ a_s a_r, \tag{2.29}$$

where a_p^+ is a creation operator which creates an electron in spin orbital ψ_p, and a_q is an annihilation operator which removes an electron from spin orbital ψ_q. These creation and annihilation operators fulfill the anticommutation relations

$$[a_p^+, a_q^+]_+ = 0, \quad [a_p, a_q]_+ = 0, \quad [a_p, a_q^+]_+ = \delta_{pq}. \tag{2.30}$$

By observing Eqn.(2.29) and one can see that the integrals h_{pq} and $\langle pq||rs\rangle$ appear as parameters. If the choice of parameters is based on Eqs.(2.13), (2.14), and (2.15) then the procedure is called *ab initio*. On the other hand, one can find suitable parameters to replace the integrals in the *ab initio* method, and yet give results of the molecular properties which fit best to either *ab initio* or experimental results. Such approaches are called semiempirical. Since many integrals can be replaced with parameters in semiempirical approaches, it is quite possible to do calculations on large molecules with such methods.

2.2.1 Hückel and Extended Hückel Methods

The first semiempirical method was developed by Hückel [13] in 1931 and is referred to as the Hückel molecular-orbital (HMO) method. HMO consists of a one-electron Hamiltonian, that takes only valence π-electrons into account. It differs from an SCF scheme, since the electron operators do not depend on the charge density.

$$H_\pi = \sum_{i=1}^{n} H^{eff}(i), \tag{2.31}$$

where n is the number of π electrons. The form of $H^{eff}(i)$ is not specified, but it satisfies the relation

$$H^{eff}(i)\psi_i = \varepsilon_i \psi_i, \tag{2.32}$$

where ψ_i is the ith π molecular orbital, and ε_i is the molecular orbital energy. HMO also assumes LCAO-MO for ψ_i:

$$\psi_i = \sum_{\mu=1}^{M} \phi_\mu c_{\mu i}, \tag{2.33}$$

where M is the number of atoms and ϕ_μ is a π atomic orbital on the μth atom. Then the variational theorem is applied and the molecular orbitals are obtained by solving the secular equation, assuming an identity overlap matrix,

$$\det|\mathbf{H}^{eff} - \varepsilon \mathbf{1}| = 0. \tag{2.34}$$

The matrix elements or integrals $H^{eff}_{\mu\nu}$ are the key assumptions of the HMO, where

$$H^{eff}_{\mu\mu} = \langle \phi_\mu | H^{eff} | \phi_\mu \rangle \equiv \alpha, \tag{2.35}$$

$$H_{\mu\nu}^{eff} = \langle\phi_\mu|H^{eff}|\phi_\nu\rangle \equiv \beta,\ \mu \text{ and } \nu \text{ bonded}$$
$$= 0,\ \mu \text{ and } \nu \text{ not bonded.} \qquad (2.36)$$

Thus the interelectronic repulsions are averaged into unspecified one-electron integrals 'Coulomb', α, and 'resonance', β, and the construction of the Hamiltonian matrix is based on molecular topology.

Later the extended Hückel theory (EHT) [14] was developed. EHT is an all-valence one-electron theory. The idea was first put forth by Mulliken in 1940s, then further developed by Wolfsberg and Helmholtz, Lohr and Lipscomb, and Hoffman. The one-electron Hamiltonian is defined as the following:

$$H_{\mu\mu}^{eff} = -V_\mu \qquad (2.37)$$
$$H_{\mu\nu}^{eff} = \frac{1}{2}K(H_{\mu\mu}^{eff} + H_{\nu\nu}^{eff})S_{\mu\nu} \qquad (2.38)$$

where V_μ is the valence shell ionization potential of atomic orbital ϕ_μ, K is a numerical constant with values between 1.75 and 3 in applications. Unlike the HMO, EHT is a method that includes overlap, so one needs to solve the secular equation with a non-identity overlap matrix,

$$\det(\mathbf{H}^{eff} - \mathbf{\Delta}\varepsilon_i) = 0. \qquad (2.39)$$

Similar to the HMO method, the early version of EHT is not an interative procedure either (however, iterative procedures have been introduced to extend the usefulness of this method). These two methods are rather valuable for conjugated organic compounds. However, for nonalternant hydrocarbons, or many systems containing heteroatoms, these methods do not even offer a qualitative description.

2.2.2 Semiempirical SCF MO Methods of the ZDO Type

Before going into details of the ZDO type methods, we would like to have our notations defined as the following: **F** for Fock matrix, and $\mathbf{F} = \mathbf{H} + \mathbf{G}$ where **H** is the one-electron matrix and **G** is the two-electron matrix. $\mathbf{G} = \mathbf{J} - \frac{1}{2}\mathbf{K}$ (close-shell), where **J** is the Coulomb integral matrix and **K** is the exchange integral matrix.

Based on the resolution of the HF equations, Pariser, Parr and Pople developed a more elaborate method (PPP) [15–18]. This method is an SCF method but still belongs to the π-electron type. Interelectronic repulsions are included in the Hamiltonian as in the Hartree-Fock method, yet similar to HMO, overlap is ignored, and further, the zero differential overlap (ZDO) approximation is made for the two electron integrals:

$$\phi_\mu^*(1)\phi_\nu(1)dv_1 = 0, \text{ for } \mu \neq \nu, \tag{2.40}$$

which results in

$$\langle\mu\lambda|\nu\sigma\rangle = \delta_{\mu\nu}\delta_{\lambda\sigma}\langle\mu\lambda|\mu\lambda\rangle \equiv \gamma_{\mu\lambda}, \tag{2.41}$$

where $\gamma_{\mu\lambda}$ are often treated as empirical parameters. Although the PPP method is not really applicable to systems other than conjugated and aromatic systems, it is a milestone in the development of quantum chemistry, since the inclusion of the interelectronic interactions is the first consistent improvement over the HMO method. Furthermore the ZDO approximation is one of the most important features for subsequent semiempirical SCF MO methods.

During the 1960s, Pople and collaborators introduced a series of ZDO methods: the complete neglect of differential overlap (CNDO) method, intermediate neglect of differential overlap (INDO) method [19–22], and the neglect of diatomic differential overlap (NDDO) method. These are all-valence-electron methods, with the overlap ignored as in PPP method. However, core integrals of the type

$$H_{\mu_A \nu_B} = \langle \mu_A | H^{core} | \nu_B \rangle \tag{2.42}$$

between non-bonded atoms are no longer ignored, as many are in the HMO method. They may be treated in a semiempirical manner in order to accomodate the possible bonding effect of overlap. The various ZDO methods outlined in the following text differ mainly in the extent to which the ZDO approximation is invoked in the calculation of inter-electronic repulsion integrals. Although the particular ZDO approximation used will be different among the various ZDO methods, the SCF procedure is the same for all: that is, the orbital energies and corresponding molecular orbitals are obtained by solving the Roothaan equation self consistently, with the overlap set to the identity matrix.

Before discussing the various methods based on the ZDO approximation, there is a condition that all these methods need to fulfill. They all need to be rotationally invariant in order to avoid unphysical results, e.g., the total energy varies as the coordinate system changes. This puts certain restriction on the matrix elements.

Complete Neglect of Differential Overlap method

As indicated in the name, complete neglect of differential overlap (CNDO), the differential overlap considered in this method follows strictly Eqn. (2.40). From this equation it follows that the two-electron integrals in the CNDO scheme are approximated as

$$\langle \mu\lambda|\nu\sigma\rangle = \gamma_{\mu\lambda}\delta_{\mu\nu}\delta_{\lambda\sigma} = \gamma_{AB}\delta_{\mu\nu}\delta_{\lambda\sigma}, \tag{2.43}$$

where orbitals ϕ_μ and ϕ_ν are centered on atom A and ϕ_λ, ϕ_σ are centered on atom B. Then the Fock matrix elements are given as the following:

$$\begin{aligned}
F_{\mu_A\mu_A} &= H_{\mu_A\mu_A} - \frac{1}{2}P_{\mu_A\mu_A}\gamma_{AA} + \sum_B P_{BB}\gamma_{AB}, && (2.44)\\
F_{\mu_A\nu_A} &= -\frac{1}{2}P_{\mu_A\nu_A}\gamma_{AA}, && (2.45)\\
F_{\mu_A\sigma_B} &= H_{\mu_A\sigma_B} - \frac{1}{2}P_{\mu_A\sigma_B}\gamma_{AB}, && (2.46)\\
P_{BB} &= \sum_{\sigma\in B} P_{\sigma\sigma}. && (2.47)
\end{aligned}$$

In these equations γ_{AB} are the Coulomb type integrals, which depends on the particular pair of atoms that are involved. γ_{AB} represents the average electrostatic repulsion between any electron on atom A and any electron on atom B, and it is made to be approximately equal to R_{AB}^{-1} as the interatomic distance R_{AB} increases. Making these two-center two-electron integrals depend on the nature of atoms A and B, and R_{AB}, maintains rotational invariance. The core operator H is defined

$$H = -\frac{1}{2}\nabla^2 - \sum_B V_B, \tag{2.48}$$

where $-V_B$ is the potential for an electron on atom A, due to the attraction from nucleus B, and the repulsion from the inner shell electrons of atom B. The matrix elements of Eqn.(2.48) in the given atomic orbitals are:

$$\begin{aligned} H_{\mu_A\mu_A} &= \langle\mu_A| -\frac{1}{2}\nabla^2 - V_A|\mu_A\rangle - \sum_{B\neq A}\langle\mu_A|V_B|\mu_A\rangle && (2.49)\\ &= U_{\mu_A\mu_A} - \sum_{B\neq A}\langle\mu_A|V_B|\mu_A\rangle, \\ H_{\mu_A\nu_A} &= U_{\mu_A\nu_A} - \sum_{B\neq A}\langle\mu_A|V_B|\nu_A\rangle = 0, && (2.50)\\ H_{\mu_A\sigma_B} &= \langle\mu_A| -\frac{1}{2}\nabla^2 - V_A - V_B|\sigma_B\rangle - \sum_{C\neq A,B}\langle\mu_A|V_C|\sigma_B\rangle && (2.51)\\ &= \beta_{\mu_A\sigma_B} = \beta^0_{AB}S_{\mu_A\sigma_B}. && (2.52) \end{aligned}$$

The text below explains the approximations for Eqs. (2.49) - (2.52). The $U_{\mu_A\mu_A}$ term in Eqn. (2.49) is a one-center term, and it contains the one-center kinetic energy and potential energy. Here the term 'potential energy' refers to the attraction with the nucleus A on which ϕ_μ is centered and the repulsion with the core electrons centered on A. This term vanishes in Eqn. (2.50) for the following reason: within the given atomic orbitals, the one-center term $U_{\mu_A\nu_A}$ becomes zero because the valence atomic orbitals ϕ_μ and ϕ_ν belonging to the same atom are orthogonal to each other. The two-center term in Eqn. (2.50), $\langle\mu_A|V_B|\nu_A\rangle$, is also zero, as the monoatomic differential overlap $\phi_\mu\phi_\nu dv_1$ is zero according to Eqn. (2.40). Finally, the term $\sum_{C\neq A,B}\langle\mu_A|V_C|\sigma_B\rangle$ in the two-center one-electron elements in Eqn. (2.51) is considered comparable to the three-center two-electron terms and should be omitted. However, the element $\langle\mu_A|-\frac{1}{2}\nabla^2 - V_A - V_B|\sigma_B\rangle$ which connects two atomic centers A

and B and therefore governs the bonding between them, is most commonly approximated with the parameter $\beta_{\mu_A\sigma_B}$, the so called 'resonance integral'. β is chosen as an atomic parameter in order to satisfy invariance conditions, and there are different choices of the forms of β^0_{AB}. One common choice is given by the Wolfsberg-Helmholtz formula [23]:

$$\beta_{\mu_A\sigma_B} = \frac{1}{2}(\beta_A + \beta_B)S_{\mu_A\sigma_B}. \tag{2.53}$$

Combining the core integrals in Eqs. (2.49) - (2.52) with the Fock matrix elements, Eqs. (2.44) - (2.46) gives

$$\begin{aligned} F_{\mu_A\mu_A} &= U_{\mu_A\mu_A} + (P_{AA} - \frac{1}{2}P_{\mu_A\mu_A})\gamma_{AA} + \sum_{B\neq A}(P_{BB}\gamma_{AB} - V_{AB}), && (2.54)\\ F_{\mu_A\nu_A} &= -\frac{1}{2}P_{\mu_A\nu_A}\gamma_{AA}, && (2.55)\\ F_{\mu_A\sigma_B} &= \beta^0_{AB}S_{\mu_A\sigma_B} - \frac{1}{2}P_{\mu_A\sigma_B}\gamma_{AB}, && (2.56)\end{aligned}$$

where

$$V_{AB} = \langle\mu_A|V_B|\mu_A\rangle. \tag{2.57}$$

Let the net charge on atom B be Q_B, then

$$Q_B = Z_B - P_{BB}, \tag{2.58}$$

and applying this charge to expression of $F_{\mu_A\mu_A}$ gives

$$F_{\mu_A\mu_A} = U_{\mu_A\mu_A} + (P_{AA} - \frac{1}{2}P_{\mu_A\mu_A})\gamma_{AA} + \sum_{B\neq A}[-Q_B\gamma_{AB} + (Z_B\gamma_{AB} - V_{AB})]. \tag{2.59}$$

A widely used approximation which can be understood from the rearranged expression above, was introduced to the two-center Fock matrix element. The first part, $Q_B\gamma_{AB}$, respresents the potential that arises from the total charge on atom B, and the second part,

$$Z_B\gamma_{AB} - V_{AB}, \tag{2.60}$$

is referred as the penetration integral following Goeppert-Mayer and Sklar [24]. In most of the parameterization schemes, the penetration integrals are normally considered to be zero in order to compensate for corrections that are needed in the ZDO approximation, and hence this leads to

$$F_{\mu_A\mu_A} = U_{\mu_A\mu_A} + (P_{AA} - \frac{1}{2}P_{\mu_A\mu_A})\gamma_{AA} + \sum_{B\neq A}(P_{BB} - Z_B)\gamma_{AB}. \tag{2.61}$$

There are many different parameterization schemes used with the CNDO Hamiltonian, but these will not be reviewed here. However, due to the similarity between CNDO and INDO, some of the details will be mentioned later together with those schemes for the INDO method.

Intermediate Neglect of Differential Overlap method

The Hamiltonian of the intermediate neglect of differential overlap (INDO) method is similar to the CNDO Hamiltonian. The major difference is that one-center two-electron integrals of the type $\langle\mu_A\sigma_A|\nu_A\lambda_A\rangle$ are retained.

The one-center one-electron integral elements of the INDO Hamiltonian are

$$\begin{aligned} H_{\mu_A\mu_A} &= \langle\mu_A| -\frac{1}{2}\nabla^2 - V_A|\mu_A\rangle - \sum_{B\neq A}\langle\mu_A|V_B|\mu_A\rangle \\ &= U_{\mu\mu} - \sum_{B\neq A} V_{AB}, \end{aligned} \tag{2.62}$$

where ϕ_μ is centered on atom A. $U_{\mu\mu}$ is the atomic core integral, which stands for the one-center kinetic energy, attraction with the nucleus, and repulsion with the core electrons on the same center, in the same way as it is defined in the CNDO method, similarly for the term V_{AB}. Also the two-center core integrals are approximated the same way, and if the Wolfsberg-Helmholtz formula [23] is adopted one obtains:

$$H_{\mu_A\nu_B} = \frac{1}{2}(\beta_A + \beta_B)S_{\mu_A\nu_B}, \tag{2.63}$$

where β_A, β_B are empirical parameters for atom A and atom B respectively.

The diagonal one-center two-electron integral elements are

$$G_{\mu_A\mu_A} = \sum_{\lambda_A\sigma_A} P_{\lambda_A\sigma_A}[\langle\mu_A\lambda_A|\mu_A\sigma_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\sigma_A\mu_A\rangle] + \sum_{B\neq A} P_{BB}\gamma_{AB}, \tag{2.64}$$

where

$$P_{BB} = \sum_{\lambda\in B} P_{\lambda\lambda}. \tag{2.65}$$

It is important that the parameterization of γ_{AB} satisfies the rotational invariance condition. In a basis set with s- and p- functions only, Eqn. (2.64) becomes

$$G_{\mu_A\mu_A} = \sum_{\lambda_A} P_{\lambda_A\lambda_A}[\langle\mu_A\lambda_A|\mu_A\lambda_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\lambda_A\mu_A\rangle] + \sum_{B\neq A} P_{BB}\gamma_{AB}. \tag{2.66}$$

The off-diagonal one-center two-electron integral elements are,

$$\begin{aligned} G_{\mu_A\nu_A} &= \sum_{\lambda_A\sigma_A} P_{\lambda_A\sigma_A}[\langle\mu_A\lambda_A|\nu_A\sigma_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\sigma_A\nu_A\rangle], \\ &= \frac{1}{2}P_{\mu_A\nu_A}[3\langle\mu_A\nu_A|\nu_A\mu_A\rangle - \langle\mu_A\nu_A|\mu_A\nu_A\rangle], \end{aligned} \tag{2.67}$$

where the second equality holds when only s- and p- types orbitals are involved. Many of these integrals are absent in CNDO and thus constitutes the main difference between CNDO and INDO.

Finally, there are the two-center two-electron integral elements, which are exchange type of integrals because of the ZDO approximation:

$$G_{\mu_A\sigma_B} = -\frac{1}{2}P_{\mu_A\sigma_B}\gamma_{AB}, \tag{2.68}$$

where orbital ϕ_μ is centered on atom A and ϕ_σ is centered on atom B. Combining both the one-electron and the two-electron matrix elements we get the Fock matrix elements for the INDO method (with s- and p- orbitals only in the basis set):

$$F_{\mu_A\mu_A} = U_{\mu_A\mu_A} + \sum_{\lambda_A} P_{\lambda_A\lambda_A}[\langle\mu_A\lambda_A|\mu_A\lambda_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\lambda_A\mu_A\rangle]$$

$$+\sum_{B\neq A}(P_{BB}\gamma_{AB}-V_{AB}), \tag{2.69}$$

$$F_{\mu_A\nu_A} = \frac{1}{2}P_{\mu_A\nu_A}[3\langle\mu_A\nu_A|\nu_A\mu_A\rangle - \langle\mu_A\nu_A|\mu_A\nu_A\rangle], \tag{2.70}$$

$$F_{\mu_A\sigma_B} = \beta^0_{AB}S_{\mu_A\sigma_B} - \frac{1}{2}P_{\mu_A\sigma_B}\gamma_{AB}. \tag{2.71}$$

Again, following the Goeppert-Mayer-Sklar approximation by using Eqn. (2.58), one can rewrite the two center part of $F_{\mu_A\mu_A}$ into the penetration integrals, $Z_B\gamma_{AB}-V_{AB}$, and $-Q_B\gamma_{AB}$, and ignore the penetration integrals. This is done in most of the INDO schemes and leads to an expression similar to Eqn. (2.61):

$$\begin{aligned} F_{\mu_A\mu_A} &= U_{\mu_A\mu_A} + \sum_{\lambda_A} P_{\lambda_A\lambda_A}[\langle\mu_A\lambda_A|\mu_A\lambda_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\lambda_A\mu_A\rangle] \\ &\quad + \sum_{B\neq A}(P_{BB}-Z_B)\gamma_{AB}, \end{aligned} \tag{2.72}$$

when using the basis set consisting of s- and p- functions only.

Neglect of Diatomic Differential Overlap method

In the NDDO method all one-center differential overlaps are included; viz.,

$$\phi^*_{\mu_A}(1)\phi_{\sigma_B}(1)dv_1 = \delta_{AB}\phi^*_{\mu_A}(1)\phi_{\sigma_A}(1)dv_1. \tag{2.73}$$

With the understanding that the main difference is in the two-electron integrals, we can write the NDDO Fock matrix elements:

$$F_{\mu_A\mu_A} = U_{\mu_A\mu_A} - \sum_{B\neq A}\langle\mu_A|V_B|\mu_A\rangle + \sum_{\nu_A\sigma_A} P_{\nu_A\sigma_A}[\langle\mu_A\nu_A|\mu_A\sigma_A\rangle \tag{2.74}$$

$$
\begin{aligned}
& -\frac{1}{2}\langle\mu_A\nu_A|\sigma_A\mu_A\rangle] + \sum_{B\neq A} P_{BB}\langle\mu_A\sigma_B|\mu_A\lambda_B\rangle, & (2.75)\\
F_{\mu_A\nu_A} &= -\sum_{B\neq A}\langle\mu_A|V_B|\nu_A\rangle + \sum_{\sigma_A\lambda_A} P_{\sigma_A\lambda_A}(\langle\mu_A\sigma_A|\nu_A\lambda_A\rangle - \frac{1}{2}\langle\mu_A\sigma_A|\lambda_A\nu_A\rangle) \\
& + \sum_{B\neq A} P_{\sigma_B\lambda_B}\langle\mu_A\sigma_B|\nu_A\lambda_B\rangle, \text{ for } \phi_{\mu_A}\neq\phi_{\nu_A} & (2.76)\\
F_{\mu_A\sigma_B} &= \beta^0_{AB}S_{\mu_A\sigma_B} - \frac{1}{2}\sum_{\nu_A\lambda_B} P_{\nu_A\lambda_B}\langle\mu_A\sigma_B|\nu_A\lambda_B\rangle. & (2.77)
\end{aligned}
$$

The potential $\langle\mu_A|V_B|\nu_A\rangle$ is divided into four groups and calculated according to the Goeppert-Mayer-Sklar approximation [24]:

$$
\begin{aligned}
\langle s_A|V_B|s_A\rangle &= Z_B^*\langle s_As_B|s_As_B\rangle, & (2.78)\\
\langle s_A|V_B|p\sigma_A\rangle &= Z_B^*\langle s_As_B|p\sigma_As_B\rangle, & (2.79)\\
\langle p\sigma_A|V_B|p\sigma_A\rangle &= Z_B^*\langle p\sigma_As_B|p\sigma_As_B\rangle, & (2.80)\\
\langle p\pi_A|V_B|p\pi_A\rangle &= Z_B^*\langle p\pi_As_B|p\pi_As_B\rangle. & (2.81)
\end{aligned}
$$

Z_B^* in the expressions above is the effective core charge, which is obtained by subtracting the number of the core electrons from the atomic number in order to be consistent with the valence-electrons only method, and reflects the effect of screening the nucleus from the valence electrons by the core ones.

The two-center two-electron integrals in Eqn. (2.77) are particular for the NDDO method, $\langle\mu_A\sigma_B|\nu_A\lambda_B\rangle$, and they can be evaluated theoretically using Slater type orbitals or by a parameterization scheme by Dewar, the modified-NDDO (MNDO) method [25, 26]. In this case the integrals are obtained by doing a multipole-multipole expansion of the corresponding integrals [27, 28]:

$$\langle \mu_A \sigma_B | \nu_A \lambda_B \rangle = \sum_{l_1, l_2, m} [M^A_{l_1,m} M^B_{l_2,m}], \tag{2.82}$$

where $M_{l,m}$ is the 2^l-pole moment of the charge distribution arising from the corresponding atomic orbital product, and the subscripts l, and m correspond to the order and the orientation of the given multipole. Each multipole can be represented by an appropriate configuration of 2^l point charges, the multipole interaction energy can be calculated by the following function,

$$[M^A_{l_1,m} M^B_{l_2,m}] = \frac{1}{2^{l_1+l_2}} \sum_{i=1}^{2l_1} \sum_{j=1}^{2l_2} \{R^2_{ij} + [(\rho^A_{l_1} + \rho^B_{l_2})^2]\}^{-1/2}, \tag{2.83}$$

where the parameters $\rho^A_{l_1}$ and $\rho^B_{l_2}$ are set by the limit at $R_{AB} = 0$. Clearly as $R_{AB} \to \infty$, the function approaches $1/R_{AB}$

2.2.3 Parameterization for the INDO Method

The main concern in this work is to find a method useful for both geometry and electronic excitation calculations. The general INDO Hamiltonian has been outlined earlier in the text. However, there are many versions of the INDO method all using different parameterization schemes. It is appropriate to outline briefly the most important parameterization schemes before I proceed to discuss my own work.

INDO parameterization

The INDO parameterization is similar to the scheme for CNDO/1 or CNDO/2. The integrals that are parameterized are the overlap integrals, $S_{\mu\nu}$, the core Hamiltonian integrals $U_{\mu\mu}$, V_{AB}, the resonance integrals β^0_{AB}, and the two-electron repulsion integrals γ_{AA} and γ_{AB}. For the INDO model, also all the one-center two-electron integrals are required, which is the difference compared to CNDO model. The basis set for the valence shell consists of Slater type orbitals [29]:

$$\phi_{nlm} = \frac{[2\xi/a_0]^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\xi r/a_0} Y_l^m(\theta, \phi), \tag{2.84}$$

where ξ is the orbital exponent calculated according to Slater rules [29] (except for hydrogen, where ξ=1.2 is used as this value is more appropriate for hydrogen in molecules), a_0 is the Bohr radius, n is the principle quantum number, l is the angular quantum number, m is the magnetic quantum number, $Y_l^m(\theta, \phi)$ are the spherical harmonics, and (r, θ, ϕ) are the spherical polar coordinates. The one-center basis functions are orthogonal to each other, except, for example, the Slater s functions from different shells are not orthogonal to each other because of the lack of the nodes in the radial part. However, since only the valence shell is considered in the all-valence semiempirical methods, no problem arises from this feature. The overlap integrals are explicitely calculated. The two-center two-electron integral γ_{AB}, which is treated as an average interaction between electrons in the valence orbitals on atom A and B, is evaluated as two-center Coulomb integrals using the s-orbital but use the exponents of the corresponding orbitals (as was done in SINDO1 [30]) in order to preserve the radial extent:

$$\gamma_{AB} = \int \int s_A^2(1) \frac{1}{r_{12}} s_B^2(2) dv_1 dv_2, \tag{2.85}$$

and the one-center two-electron integrals γ_{AA} are also calculated *ab initio* too.

The potential energy involving a valence electron on atom A with the core electrons and the nucleus of atom B, V_{AB}, is calculated from the following equation in the CNDO/1 scheme,

$$V_{AB} = Z_B \int s_A^*(1) \frac{1}{r_{1B}} s_A(1) dv_1, \tag{2.86}$$

where Z_B is the core charge of atom B and r_{1B} is the distance of electron 1 from the nucleus B. An effective core charge Z_B^* is introduced:

$$Z_B^* = Z_B - n_B^{core}, \tag{2.87}$$

where n_B^{core} is the number of core electrons on atom B. The effective core charge provides the screening effect exerted by the core electrons so that the valence electrons feel the attraction from a nucleus with only the effective core charge. We replace the core charge in the calculation of V_{AB} with the effective core charge. The equilibrium bond lengths obtained from the CNDO/1 method tend to be too short, and the dissociation energies tend to be too large. The error comes partly from the penetration integrals, and partly from the nature of the ZDO approximation. The problem can be resolved by ignoring the penetration integrals, i.e., according to the Goeppert-Mayer-Sklar approximation [24], the evaluation of V_{AB} becomes

$$V_{AB} = \langle \mu_A | V_B | \mu_A \rangle = Z_B^* \gamma_{AB}. \tag{2.88}$$

This is implemented in the CNDO/2, INDO/1 and INDO/S parameterizations as well.

For the resonance integral β_{AB}^0, the Wolfsberg-Helmholtz formula [23] is applied,

$$\beta_{AB}^0 = \frac{1}{2}(\beta_A + \beta_B), \tag{2.89}$$

where β_I is an empirical parameter specific for atom I.

The core integrals $U_{\mu\mu}$ contain the one-center kinetic energy and the core potential. These integrals are obtained from the observed atomic energy levels. For an atom A with electron configuration $(2s)^m(2p)^n$, the total energy within the CNDO approximation is given by [19]

$$E(X, 2s^m 2p^n) = mU_{2s2s} + nU_{2p2p} + \frac{(m+n)!}{2!(m+n-2)!}\gamma_{AA}, \tag{2.90}$$

where X is the filled core. When one p-electron is taken away, the total energy becomes

$$E(X, 2s^m 2p^{n-1}) = mU_{2s2s} + (n-1)U_{2p2p} + \frac{(m+n-1)!}{2!(m+n-3)!}\gamma_{AA}. \tag{2.91}$$

Ignoring orbital relaxation after the loss of one electron, the ionization potential derived from this scheme is

$$\begin{aligned} I_p &= E(X, 2s^m 2p^{n-1}) - E(X, 2s^m 2p^n) \\ &= -U_{2p2p} - (m+n-1)\gamma_{AA}, \end{aligned} \tag{2.92}$$

and therefore the core integrals U_{2s2s} and U_{2p2p} are obtained by the expression below:

$$U_{\mu_A \mu_A} = -I_{\mu_A} - (Z_A^* - 1)\gamma_{AA}. \tag{2.93}$$

Using merely the ionization energy to calculate the core integral $U_{\mu\mu}$ is the strategy adopted for the CNDO/1, INDO/2, and INDO/S methods. However, in order to account for the ability of an atomic orbital to both aquire and lose electrons, both the ionization potential and the electron affinity are used in CNDO/2 and are related to $U_{\mu\mu}$ through

$$-\frac{1}{2}(I_{\mu_A} + A_{\mu_A}) = U_{\mu_A \mu_A} + (Z_A^* - \frac{1}{2})\gamma_{AA}, \tag{2.94}$$

which is obtained by combining Eqn. (2.93) and the following:

$$U_{\mu_A \mu_A} = -A_{\mu_A} - Z_A^* \gamma_{AA}, \tag{2.95}$$

where A_{μ_A} is the electron affinity of the atomic orbital ϕ_μ on atom A. This way of employing the ionization potential and electron affinity into the determination of core integrals assumes frozen orbitals upon losing or obtaining an electron, as shown in Eqn. (2.94). As discussed previously Koopmans' theorem is a good approximation for ionization potential but not for the electron affinity. Therefore, it may not be a surprise that CNDO/2 does not predict ionization potentials very well. For the one-center two-electron integrals in the INDO method, the Slater-Condon parameters [31, 32] F^0, G^1, and F^2, which are two-electron integrals involving the radial parts of the atomic orbitals, are used to evaluate the related integrals:

$$\begin{aligned}
\langle ss|ss\rangle &= \langle sp_x|sp_x\rangle = F_A^0 = \gamma_{AA}, && (2.96)\\
\langle ss|p_xp_x\rangle &= \frac{1}{3}G_A^1, && (2.97)\\
\langle p_xp_x|p_yp_y\rangle &= \frac{3}{25}F_A^2, && (2.98)\\
\langle p_xp_x|p_xp_x\rangle &= F_A^0 + \frac{4}{25}F_A^2, && (2.99)\\
\langle p_xp_y|p_xp_y\rangle &= F_A^0 - \frac{2}{25}F_A^2. && (2.100)
\end{aligned}$$

These one-center two-electron terms in the INDO method make the evaluation of core integrals $U_{\mu\mu}$ more complicated than in CNDO, since in the INDO scheme, the total energy for an atom A with electron configuration $(2s)^m(2p)^n$ becomes [21]

$$\begin{aligned}
E(X, 2s^m 2p^n) &= mU_{2s2s} + nU_{2p2p} + \frac{(m+n)(m+n-1)}{2}F^0 \\
&- \frac{1}{6}mnG^1 - \frac{1}{25}n(n-1)F^2. && (2.101)
\end{aligned}$$

For example, if similar parameterization scheme as CNDO/2 is followed, then for the elements B to F in the second row, $U_{2p,2p}$ is given within INDO (i.e., INDO/2) by

$$U_{2p2p} = -\frac{(I_{2p} + A_{2p})}{2} - (Z^* - 1/2)F_A^0 + \frac{1}{3}G_A^1 + \frac{2}{25}(Z^* - 5/2)F_A^2, \tag{2.102}$$

where $Z^* = m + n$ is the effective core charge.

Within the Born-Oppenheimer approximation, the nuclear-nuclear repulsion potential needs to be added to the electronic energy to obtain the total energy. For the all-valence methods, the compatible nuclear-nuclear repulsion is evaluated using the effective core charge. This can be illustrated using the case of a simple diatomic molecule with the numbers of core electrons being n_A and n_B. We assume that the core electrons are rather localized and hence the electron exchange between the cores are ignored:

$$\begin{aligned} E_{nu-nu} &= \frac{Z_A Z_B}{R_{AB}} - \frac{n_A Z_B}{R_{AB}} - \frac{n_B Z_A}{R_{AB}} + \frac{n_A n_B}{R_{AB}} \\ &= \frac{Z_A^* Z_B^*}{R_{AB}}. \end{aligned} \tag{2.103}$$

The total energy is thus calculated from

$$E_{total} = E_{elec} + \sum_{A>B} \frac{Z_A^* Z_B^*}{R_{AB}}. \tag{2.104}$$

INDO/S and CNDO/S parameterization

Inspired by an observation of Pariser's [18] concerning the two-electron integrals in the PPP method, Jaffé and Del Bene modified the CNDO/2 parameters [33–35], which made it possible to utilize the semiempirical method for electronic spectra calculations. According to Pariser, the one-center two-electron integrals are given by

$$\gamma_{\mu_A \mu_A} = I_{\mu_A} - A_{\mu_A}, \tag{2.105}$$

where A_{μ_A} is the electron affinity of atomic orbital ϕ_μ. For the two-center two-electron integrals, at first they used the Pariser-Parr formula [17]:

$$\gamma_{AB} = \frac{1}{2}(\gamma_A + \gamma_B) - aR_{AB} - bR_{AB}^2, \tag{2.106}$$

in which a, and b are constants that are determined for R_{AB} between 2.8 Å and 3.7 Å. Later suggested by Zerner and Ridley in their INDO/S method (see below), these integrals were evaluated using the Mataga-Nishimoto formula [36]:

$$\gamma_{AB} = \frac{1}{a + R_{AB}}, \tag{2.107}$$

where a is the inverse of the average of the one-center two-electron integrals of atoms A, and B:

$$a = \frac{2}{\gamma_{\mu_A} + \gamma_{\sigma_B}}, \tag{2.108}$$

The expression of the resonance integral is also modified

$$\beta_{\mu_A\sigma_B} = \frac{1}{2}(\beta_A + \beta_B)S'_{\mu_A\sigma_B}, \tag{2.109}$$

where the overlap matrix element is modified according to

$$\begin{aligned} S'_{\mu_A\sigma_B} &= \sum_l g_l f_l \langle \mu_{l_A} | \sigma_{l_B} \rangle \\ &= g_\sigma f_\sigma \langle \mu_{\sigma_A} | \sigma_{\sigma_B} \rangle + (g_\pi + g_{\pi'}) f_\pi \langle \mu_{\pi_A} | \sigma_{\pi_B} \rangle + \cdots, \end{aligned} \tag{2.110}$$

where the factors g_l are the Eulerian rotational factors necessary in evaluating the integrals in the local coordinate system and transforming back to the molecular coordinate system. The parameter f is to remedy the problem in CNDO/2 of overestimating the interactions among π bonding orbitals, compared to σ bonding orbitals. The optimized values for f are:

$$f_\sigma = 1.0, \tag{2.111}$$

$$f_\pi = 0.585. \tag{2.112}$$

In the 1970's, Zerner and Ridley [37, 38] developed the spectroscopy version of INDO method, called INDO/S, by modifying the INDO parameters. Similar to what was done in CNDO/S, the one-center two-electron integrals are calculated from the experimental ionization potentials and electron affinities. Different weighting factors

$$
\begin{aligned}
f_{\sigma(s)} &= 1.0, && (2.113)\\
f_{\pi} &= 0.585, && (2.114)\\
f_{\sigma(p)} &= 1.267, && (2.115)
\end{aligned}
$$

are applied to the overlap between different types of molecular orbitals when constructing two-center one-electron integral as in Eqn. (2.109).

The Mataga-Nishimoto form of the two-center two-electron integrals is adopted, as in CNDO/S, but the Weiss parameter $f_y = 1.2$ is found to yield better results for calculations of spectroscopic properties of large molecules:

$$\gamma_{AB} = \frac{f_y}{((\gamma_A + \gamma_B)/2f_y)^{-1} + R_{AB}}. \tag{2.116}$$

Moreover, the Slater-Condon factors are from atomic spectroscopic data in order to be compatible with the one-center $\gamma_{\mu\mu}$ integrals. It turns out that the experimental Slater-Condon factors are about 0.6 times the corresponding *ab initio* values. The parameterization of INDO/S was carried out at the single-excitation CI (CIS) level and based on experimental spectra. The corresponding nuclear-nuclear repulsion potential for calculating the total energy is evaluated in terms of the two-center two-electron integrals and the effective core charges:

$$E_{nu-nu} = \sum_{A>B} Z_A^* Z_B^* \gamma_{AB}. \tag{2.117}$$

So far as one can find from the literature, all the integrals which are used in the spectroscopic version of ZDO methods are smaller in magnitude than those which are used in the corresponding *ab initio* case. This is due to two factors: dynamic electron correlation and the effect which is caused by using the minimal basis set in the model. Including electron correlation or employing big basis set reduces the effective magnitude of the *ab initio* integrals.

A comparison between the repulsion using the Ohno-Klopman formula, the Coulomb form and the STO two-electron integral (the exponent of C is set to 1.625) is shown in Fig. 2.1. The asymptotic values at $R = 0$, γ, in the case of the C_2 molecule is indicated in the figure.

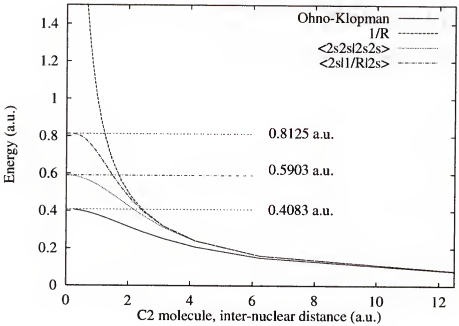

Figure 2.1. Comparison between Ohno-Klopman, Coulomb repulsion, and Slater two-electron integral

2.2.4 General Remarks

The INDO model has several advantages over CNDO in that the INDO method can separate $n \rightarrow \pi^*$ triplet and singlet states successfully because of the inclusion of one-center two-electron integrals. For example, the singlet-singlet excitation from an occupied orbital i to a virtual orbital f is

$$\Delta E_{if} = \varepsilon_f - \varepsilon_i - J_{if} + 2K_{if}, \tag{2.118}$$

and the excitation energy from orbital i to f resulting in a triplet state is

$$\Delta E_{if} = \varepsilon_f - \varepsilon_i - J_{if}, \tag{2.119}$$

where J and K are the molecular Coulomb and exchange integrals respectively. In a CNDO/S calculation, these two types of excitations are degenerate as $K_{if} = K_{n\pi} = 0$. In addition, CNDO is useless in the calculation of transition metal systems as these neglected exchange integrals are often of the order of an atomic unit [39]. However, for calculating bond lengths, bond angles, and electron density distributions, INDO does not offer too much of an improvment over CNDO. NDDO, on the other hand, by including two-center two-electron integrals, $\langle \mu_A \lambda_B | \nu_A \sigma_B \rangle$, has the potential to be superior to the original INDO method for calculating geometries and directional properties, and thus predicting, e.g., molecular dipole moments. It is not clear, however, whether this potential is realized as SINDO [30], an INDO-based model, seems as effective as AM1 [40] (an NDDO method) in predicting geometries and thermochemistry. Although many different parameterization schemes have been proposed in the past, none of them can be considered accurate enough for all molecular properties. That is to say that either the choices of parameters are not optimal, or the model Hamiltonian is not accurate, and therefore the applicability of current semiempirical methods often depends on the purpose and the means for which the model is applied.

Table 2.1. The comparison of all-valence electron methods

Method	Geometry	Charge distribution	Electronic excitation
CNDO/2	good	good	poor
CNDO/S	not app.	poor	good
INDO	good	good	poor
INDO/S	not app.	good	good
MINDO/3	good	good	poor
MNDO	good	good	poor
AM1 [40]	good	poor	poor
PM3 [41]	good	poor	poor

NOTE: All comments are from [42], except for CNDO/S, INDO/S, AM1, and PM3.

It is clear from the comments on the performance of major semiempirical methods that not many of them are good for calculating electronic spectra. Furthermore, the only two methods which are good for calculating spectra are bad for geometry optimization. Hence, this gives a strong motivation to the author to accomplish a new semiempirical model which is multi-purposed, especially equipped with the ability of calculating both electronic excitation and geometry, and thus applicable to problems in photochemistry.

CHAPTER 3
XINDO

3.1 Features

The XINDO method is designed to be applicable to both geometry and electronic excitation calculations. A common set of parameters will be sought. As stated in the theory review in the previous chapter, current existing methods are not able to yield both excitation energies and geometries equally well with a single set of parameters. Among those methods, the INDO/S method has been used to calculate molecular spectra quite successfully, but this is not the case for the other similar method, the INDO/1. On the other hand, the INDO/1 method gives good molecular geometries but the INDO/S method does not. The main difference between these two methods is the choice of two-electron integrals. Therefore, a promising approach is to understand the reason why the INDO/S method is not good for calculating geometries. Then one can take advantage of the INDO/S model which has proven good for electronic excitation calculations, and adjust it to also yield good molecular geometries.

We use the INDO/S two-electron integrals for the XINDO method, since the INDO/S method has been successful in electronic excitation calculations, and the key reason is the adoption of empirical parameters for the two-electron integrals. However, the development so far, only applies to basis set with *s*- and *p*- type orbitals.

With INDO/S as the starting point, the modifications listed below are made in order to obtain a new method which can be used to calculate geometry:

1. penetration integrals (expression (2.60)) are included by using a separate parameter for evaluating the nuclear-electron attraction.
2. an effective core potential (ECP) [43] is added to provide a short range repulsion between core electrons and valence electrons. This repulsion has much sharper distance dependence at short interatomic distance than the overlap. ECP can be used to compensate the possible drawback arising from the inclusion of the penetration integrals.
3. off-diagonal kinetic energy elements are included. Again, the distance dependence is also very different than the overlap.
4. two-center one- and two-electron integrals are approximated using the Mulliken approximation [44] together with the diagonal one- and two-electron integrals, respectively.
5. in the spirit of the EHT, XINDO will include overlap and solve the secular equation with non-identity overlap.
6. the STO Coulomb matrix is constructed with the LTO density matrix. This allows us to use the ZDO approximation (INDO or NDDO) to avoid calculating complex 3- and 4-centered integrals.
7. the nuclear-electron integrals are used for evaluating the nuclear-nuclear repulsion energy.

Besides yielding both geometry and spectra, there are some other useful features arising from the way we design XINDO: the inclusion of

1. overlap improves the description of the energies of the antibonding molecular orbitals,
2. multi-center integrals improve the description of conformational properties, dipole moment, etc..

In the following section, the details of the work and the rationale of the modifications will be given.

3.2 Details of Building XINDO

3.2.1 Comparison with Previous Models

It is natural to look into the ZDO approximation and the Hückel type methods once more. Doing so, one may understand what causes the constraint of having to choose between spectroscopic properties or geometry in the ZDO-based methods, and one may also find useful approximations for our method development.

EHT

The EHT [14] method is a one-electron theory, i.e., without two-electron integrals in the Fock matrix. Therefore EHT is not ideal for calculating the electrostatic properties. However, since the overlap matrix is not set to identity in EHT, it is able to account for the shapes of orbitals, and hence benefits the calculations of molecular geometries. The use of the overlap matrix also allows the unsymmetric energy splitting of the bonding and antibonding MO's as described below.

Consider a two-orbital homonuclear EHT Hamiltonian matrix:

$$H = \begin{vmatrix} H_{11} & H_{12} \\ H_{12} & H_{11} \end{vmatrix}. \tag{3.1}$$

From this Hamiltonian and the secular equation Eqn. (2.18), one obtains the orbital energies,

$$\varepsilon = \frac{H_{11} \pm H_{12}}{1 \pm S_{12}}. \tag{3.2}$$

If the ZDO approximation is applied in the above expression, $S_{12} = 0$, then the molecular orbitals are formed with a symmetric split from the constituent atomic orbitals, which makes the antibonding orbital higher in energy than the bonding orbital by $2|H_{12}|$. Consider now the situation where the overlap between the diffuse atomic orbitals approaches 1. In such a case the antibonding orbital is elevated in energy far greater than $2|H_{12}|$, and the bonding MO is depressed to a much less degree. This can be understood from Eqn. (3.2), as the denominator approaches zero, the antibonding MO energy increases dramatically. The illustration given here, and shown in Fig. 3.1, indicates that the overlap elements should be included to improve on the energy gap between bonding and antibonding orbitals. The inclusion of the overlap also allows the eventual use of better than a minimal basis set, as one-center overlap is also included. Therefore, one obvious way to improve on the INDO method is to express the XINDO Hamiltonian and the parameterization in a non-orthogonalized basis set, e.g., the STOs, and then solve the secular equation with a non-identity overlap matrix.

ZDO methods

CNDO/S and INDO/S methods are among the very few semiempirical methods which can calculate electronic spectroscopic properties. However, neither can be used to calculate molecular geometries. As mentioned earlier, the CNDO/S method cannot calculate transition metal systems correctly but INDO/S can, also the INDO/S can distinguish the singlet to singlet state electronic excitation from the singlet to triplet state excitation in the cases of $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ excitations. Therefore we will deal with the INDO/S model rather than CNDO. Another method at the INDO level, the INDO/1 method, gives satisfactory molecular geometries, but not electronic excitations. The main difference between the INDO/S and INDO/1 methods are the two-electron integrals. The two-electron integrals that are used in the INDO/1 method are evaluated *ab initio* over STOs; the ones that are used in the INDO/S method are evaluated according to Pariser [18] from atomic experimental data. Obviously such integrals contain electron correlation and compensate for the effects of the use of a minimal basis set, and thus make the calculations of electronic spectra possible. However, the reason why INDO/S cannot be used to calculate geometry is still unclear.

Recall the commonly used Goeppert-Mayer-Sklar approximation [24] in all ZDO methods. In that approximation, the penetration integral $Z_B\gamma_{AB} - V_{AB}$ is neglected. V_{AB} denotes the net attraction between an electron centered on atom A and nucleus B. $Z_B\gamma_{AB}$ denotes the repulsion between the same electron on atom A and the electrons on atom B. Applying this approximation means that one calculates the nuclear-electron attraction by using the two-electron integral γ_{AB}. And in the case of INDO/S, this approximation imposes the same extent of electron correlation and minimal basis set effect on both the two-electron integral and the nuclear-electron integral. An unnessary constraint may occur from such assumption.

To date, there is no report of electronic excitation calculations using the NDDO method. However, this method may have some advantages in geometry calculation because it contains the two-center two-electron integrals $\langle \mu_A \sigma_B | \nu_A \lambda_B \rangle$. The only two-center two-electron integrals existing in the INDO methods are of the exchange type. The fact that the INDO methods tend to overestimate the stabilization of ring forms over bent or linear forms for certain molecules indicates that it may be necessary to include these two-center two-electron Coulomb integrals to remedy this deficiency in the INDO methods. However, we note the success of the SINDO model which is an INDO model, with reported equal accuracy to the AM1 and PM3 methods and both are NDDO models.

3.2.2 Integral by Integral

In this section, all integrals that enter the XINDO Fock matrix will be discussed. The XINDO method is constructed in the STO representation, which is different from all other ZDO methods. Therefore, we want to know how the same Hamiltonian differs in the STO representation and in the ZDO-compatible representation.

The ZDO approximation is often justified by expressing the Hamiltonian in the Löwdin symmetric orthogonalized basis [45, 46]. We therefore will study the differences with the one-electron and two-electron integrals in these two different basis sets, STOs and LTOs.

The Löwdin type orbitals have the important property that

$$\langle \chi_\mu^{LTO} | \chi_\nu^{LTO} \rangle = \delta_{\mu\nu}, \tag{3.3}$$

and yet these orbitals resemble the orginal nonorthogonal atomic orbitals as much as possible in the least-square sense, i.e.,

$$\sum_\mu [\int (\chi_\mu^{*LTO} - \chi_\mu^*)(\chi_\mu^{LTO} - \chi_\mu) dv] = min. \tag{3.4}$$

One may transform STOs to LTOs by the following expression:

$$\mathbf{X}^{LTO} = \mathbf{\Phi}^{STO} \mathbf{\Delta}^{-1/2}, \tag{3.5}$$

where $\mathbf{\Delta} = \mathbf{1} + \mathbf{S}$ is the overlap matrix of the STOs. It is clear that the differential integral matrix between the LTOs is the identity matrix.

$$\begin{aligned} \mathbf{X}^{LTO\dagger} \mathbf{X}^{LTO} &= \mathbf{\Delta}^{-1/2} \mathbf{\Phi}^{STO\dagger} \mathbf{\Phi}^{STO} \mathbf{\Delta}^{-1/2} \\ &= \mathbf{1}, \end{aligned} \tag{3.6}$$

which is consistent with one of the ZDO approximations. As far as the two-electron integrals which are retained in the ZDO schemes are concerned, no drastic change shows up when they undergo symmertic orthogonalization transformation. It also seems a reasonable assumption that by applying empirical parameters to these integrals, the small changes introduced by the transformation from the STO to LTO basis may be taken care of. Moreover, with a symmetrically orthogonalized basis set, the electron-repulsion integrals neglected in the ZDO schemes are generally found to be quite small [47].

The effects caused by orthogonalization transformation of the one-electron Hamiltonian matrix are illustrated by the following expressions.

$$\mathbf{H}^{LTO} = \mathbf{\Delta}^{-1/2}\mathbf{H}^{STO}\mathbf{\Delta}^{-1/2}, \tag{3.7}$$

which, in the case of a two orbitals of, for example, a diatomic molecule, leads to the following:

$$\begin{aligned}
H_{\mu\mu}^{LTO} &= H_{\mu\mu}^{STO} - S_{\mu\nu}M_{\mu\nu}/(1-S_{\mu\nu}^2) && (3.8)\\
H_{\mu\nu}^{LTO} &= M_{\mu\nu}/(1-S_{\mu\nu}^2) && (3.9)\\
M_{\mu\nu} &= H_{\mu\nu}^{STO} - S_{\mu\nu}(H_{\mu\mu}^{STO} + H_{\nu\nu}^{STO}) && (3.10)\\
H_{\mu\mu}^{LTO} &= H_{\mu\mu}^{STO} - S_{\mu\nu}H_{\mu\nu}^{LTO}, && (3.11)
\end{aligned}$$

where orbital ϕ_μ is on atom A, and ϕ_ν is on atom B. Assume that the difference between H^{LTO} and H^{STO} introduced by this orbital transformation is the orthogonalization correction. Numerical results show that such correction for diagonal elements $|H_{\mu\mu}^{LTO} - H_{\mu\mu}^{STO}|$ is small, but the off diagonal elements $H_{\mu\nu}^{STO}$ and $|H_{\mu\nu}^{LTO} - H_{\mu\nu}^{STO}|$ are of similar magnitude, since $|H_{\mu\nu}^{LTO}| << |H_{\mu\nu}^{STO}|$ [48]. Thus one may conclude that the off-diagonal one-electron matrix elements of the XINDO are expected to be larger than the ones in INDO/S, but the diagonal elements should be similar in STO or LTO.

We now turn our attention to the two-electron integrals. The change in one- and two-center integrals is small when the ZDO two-electron integrals are transformed from the STO to LTO, whereas integrals involving differential diatomic overlap become quite small. Fischer-Hjalmars [49], and more recently, Thiel and Weber [50] have shown that after applying an expansion of the overlap matrix

$$\mathbf{\Delta}^{-1/2} = (\mathbf{1}+\mathbf{S})^{-1/2} = \mathbf{1} - \frac{1}{2}\mathbf{S} + \frac{3}{8}\mathbf{S}^2 - \frac{5}{16}\mathbf{S}^3 + \cdots, \tag{3.12}$$

to the right of the following expression,

$$\mathbf{G}^{LTO} = \mathbf{\Delta}^{-1/2}\mathbf{G}^{STO}\mathbf{\Delta}^{-1/2}, \tag{3.13}$$

and collecting terms up to first order in $\mathbf{S}$, the transformed integrals are exactly the same as in the non-orthogonal basis set at NDDO level. If the collected terms are up to second order in $\mathbf{S}$, then in addition to the NDDO type integrals some very small two-center integrals are introduced. Based on this observation, no obvious change in the two-electron integrals is expected. Similarly, one will not expect very different two-electron integrals in the XINDO method than other ZDO methods.

Nuclear-electron integral

From the conclusion after reviewing the ZDO methods, we decide to abandon the Goeppert-Mayer-Sklar approximation [24]. In order to do so, we will introduce a parameter for the one-center nuclear-electron attraction $\langle\mu_A|V_A|\mu_A\rangle \equiv \gamma'_{\mu_A}$. This γ'_{μ_A} will be used to calculate the two-center nuclear-electron attractions. In other words, we no longer borrow the two-center two-electron integrals to evaluate the two-center nuclear-electron attraction. Coffey [51] showed that ignoring penetration integrals was equivalent to ignoring an effective core potential and orthogonalization corrections, which are terms that we are willing to include explicitly.

The use of different weighting factors for the two-center one-electron integrals in the INDO/S method, Eqs. (2.113) - (2.115), indicates that the parameters for π and σ bonds should be different. In the XINDO, the nuclear-electron integral γ'_{μ_A} is an orbital dependent atomic parameter.

We then proceed with nuclear-electron attraction between different atoms V_{AB}. When treating two-center terms like $\langle\mu_A|V_B|\mu_A\rangle \equiv \gamma'_{\mu_A\sigma_B}$, the most important concern is to have a proper distance dependence in the proposed functional form of the parameterization that can represent the two-center interactions above. In the INDO/S model either the Mataga-Nishimoto form [36] as in Eqn. (2.107) or the Ohno-Klopman form [52, 53]

$$\gamma'_{\mu_A\nu_B} = \frac{1}{(4(\frac{1}{\gamma'_{\mu_A}} + \frac{1}{\gamma'_{\sigma_B}})^2 + R_{AB}^2)^{1/2}}, \tag{3.14}$$

is used for the two-electron interactions, and as a result, good spectra can be obtained. The Mataga-Nishimoto (MN) and the Ohno-Klopman (OK) formula have the same asymptotics. Both approach the one center limit γ'_{μ_A} or γ'_{σ_B} as $R_{AB} \rightarrow 0$, and approach zero as $R_{AB} \rightarrow \infty$. We decided to adopt the Ohno-Klopman formula to calculate the two-center two-electron integrals and the two-center core-electron terms

$$\langle \mu_A | \frac{1}{R_{AB}} | \mu_A \rangle = \gamma'_{\mu_A \sigma_B}, \tag{3.15}$$

where $\gamma'_{\mu_A \sigma_B}$ is obtained from Eqn. (3.14), because it has been shown by Zerner [37] that the MN formula cannot successfully yield both singlet and triplet excitation energies for aromatic systems. Adopting the OK formula may need higher levels of CI in reproducing singlet spectra, but the triplet spectra is readily reproduced. Finally,

$$\langle \mu_A | V_B | \mu_A \rangle = \sum_{\sigma_B} n_{\sigma_B} \gamma'_{\mu_A \sigma_B}, \tag{3.16}$$

where n_{σ_B} is the electron occupation number on atomic orbital ϕ_{σ_B}.

Two- and three-center nuclear-electron integrals

There exist two-center nuclear-electron integrals $\langle \mu_A | V_A | \sigma_B \rangle$ and also three-center $\langle \mu_A | V_{C \neq A,B} | \sigma_B \rangle$. These types of integrals are not present in the INDO methods, because the only off-diagonal one-electron integral in INDO methods are the resonance integrals β, which are empirical two-center integrals. By using the product of β and the overlap alone, the contributions from these two types of integrals are not so clear. Only in an average manner can their contributions be represented by $\beta\Delta$.

In the XINDO method, these two types of integrals are evaluated explicitly.

For any integrals which are multi-centered, the functional form assigned to them must have a proper distance dependence, in order to be compatible with the goal of obtaining good geometries. And again, from the fact that the INDO/S method has to use different weighting factors to accompany β in order to obtain good spectra, it may be better to explicitly evaluate the different parts of the off-diagonal one-electron matrix elements.

There are two options for calculating the $\langle \mu_A | V_A + V_B | \sigma_B \rangle$. The first option is based on the idea that no extra integrals need to be calculated, instead, they are obtained by applying the Mulliken approximation [44] using the diagonal one-electron Hamiltonian elements:

$$\phi_\mu^* \phi_\sigma = \frac{1}{2} S_{\mu\sigma} [\phi_\mu^* \phi_\mu + \phi_\sigma^* \phi_\sigma]. \tag{3.17}$$

The other option is to use scaled *ab initio* $\langle \mu_A | V_A + V_B | \sigma_B \rangle$ integrals. That is, the two-center nuclear-electron integrals are evaluated from first principles with the orbital exponents from Slater rules [29]. Then from the one-center nuclear-electron parameter γ'_{μ_A} the effective exponents ξ' are evaluated. Since the measure of electron-nuclear attraction is the orbital exponent, one can scale the first principles integrals by the ratios of the effective exponents ξ' and the exponents ξ from Slater rules. In that case the scaled $\langle \mu_A | V_A + V_B | \sigma_B \rangle$ integrals are compatible with the parameter γ'_{μ_A}.

The scaled *ab initio* integrals may be better than the integrals using the Mulliken approximation when, e.g., the electronegativities of the two atoms involved are very different since the Mulliken approximation will force the charge to distribute more equally between the two atoms. Another disadvantage of the Mulliken approximation is that it does not have the right asymptotics. It introduces large errors when the internuclear distance is either very small (where it may not matter) or very large. Thus, these problems may be avoided by choosing the scaled *ab initio* integrals and we decided to use such integrals.

The three-center integrals, $\langle \mu_A | V_{C \neq A,B} | \sigma_B \rangle$, are important for obtaining conformational information. These integrals can become quite sizeable with increasing molecular size, thus if we want to introduce these integrals into the INDO model, we must pay attention to the balance of the model by introducing three-center two-electron integrals as well. With the intention to avoid evaluating extra two-electron integrals, we will adopt the Mulliken approximation for these three-center integrals,

$$\langle \mu_A | \sum_{C \neq A,B} V_C | \sigma_B \rangle \approx \frac{S_{\mu\sigma}}{2} [\langle \mu_A | \sum_{C \neq A,B} V_C | \mu_A \rangle + \langle \sigma_B | \sum_{C \neq A,B} V_C | \sigma_B \rangle], \tag{3.18}$$

where $\langle \mu_A | V_C | \mu_A \rangle$ and $\langle \sigma_B | V_C | \sigma_B \rangle$ are evaluated according to Eqs. (3.16) and (3.14). The Mulliken approximation by itself is not rotational invariant. However, Eqn. (3.18) only involves empirical atomic parameters γ' and the Ohno-Klopman formula. Thus there is no angular dependence in this expression, and therefore the model remains rotational invariant.

Using the Mulliken approximation can introduce errors, as mentioned earlier, and now the error in evaluating the three-center integrals when the third center (C) is located in between the other two centers (A and B) is especially severe. We therefore will keep this in mind, and we shall add correction parameters to lessen such errors. In addition, the error in these terms should cancel against the similar error that arises in the evaluation of the two-electron terms as discussed below.

Effective core potential

Another important feature of the ZDO methods is that they are all-valence-electron methods and assume that the core electrons are very localized and will not participate in chemical reactions or low energy electronic spectroscopy. Therefore the core electrons are not included in the calculations other than modifying the core charges. However, the core electrons also repell the valence electrons which prevents them from collapsing into the core region. Hence in order to avoid such collapse that also would conflict with the Pauli principle, it is reasonable to include a short range repulsion to the system. This may improve the model so reasonable geometries may be obtained by using spectroscopic parameters. There are many studies related to the repulsion between core and valence electrons, and the use of the effective core potential (ECP) seems capable to account for such effects. For the valence-electron-only systems the following form of the ECP was derived by Zerner [43]:

$$\begin{aligned}(ECP)_{\mu_A\mu_A} &= -\sum_{\alpha_{B_{(core)}}\neq A} S_{\mu_A\alpha_B}F_{\alpha_B\alpha_B}S_{\alpha_B\mu_A} \\ &\approx -\sum_{\alpha_{B_{(core)}}\neq A} S_{\mu_A\alpha_B}\varepsilon_{\alpha_B}S_{\alpha_B\mu_A}. \qquad (3.19)\end{aligned}$$

In the last step in Eqn. (3.19), $F_{\alpha_B\alpha_B}$ is approximated with orbital energy ε_{α_B} which may be obtained from ESCA experiments [54]. This is justified from the fact that the core electrons are very localized so Koopmans' approximation may be considered good [43]. The above expression shows that this potential is proportional to the overlap squared and hence this term rises rapidly at short interatomic distance and becomes negligibly small at ranges where the bonding interaction dominates. However, through the way that INDO/S was parameterized, the ECP has been included in the diagonal one-electron integrals. The ECP contribution will be added to the off-diagonal one-electron matrix elements in the new Hamiltonian in order to fulfill the Pauli exclusion principle and the pursuit of a versatile semiempirical method. In addition, the inclusion of the ECP should improve the tendency of semiempirical models to overbind.

Off-diagonal matrix elements of the kinetic energy

The core integral $U_{\mu_A\mu_A}$ (Eqn. (2.62)) in the INDO/S method is parametrized using experimental data from atomic spectra. Therefore it already contains the ECP, nuclear-electron attraction, and also the kinetic energy. We do not need to put the kinetic energy into the diagonal part of the one-electron integrals but we are going to include it in the off-diagonal elements. This is because it has a very different distance dependence than does the overlap.

Coulomb integrals

Although we construct the XINDO method over STOs, the two-electron integrals are calculated by using the LTO density matrix and the LTO two-electron integrals.

We start the explanation for such approximation with the relationship between LTO and STO:

$$\mathbf{X}^{LTO} = \mathbf{\Phi}^{STO}\mathbf{\Delta}^{-1/2}, \tag{3.20}$$

and therefore the LCAO-MO coefficient matrices for LTO and STO will be different:

$$\begin{aligned} \mathbf{\Psi} &= (\psi_1, \psi_2, \cdots, \psi_K) = \mathbf{\Phi}^{STO}\mathbf{C} \\ &= \mathbf{X}^{LTO}\mathbf{\Delta}^{1/2}\mathbf{C} = \mathbf{X}^{LTO}\mathbf{D}, \end{aligned} \tag{3.21}$$

where K is the size of basis set, and $\mathbf{C}$, $\mathbf{D}$ are the molecular orbital coefficient matrices over STOs and LTOs, respectively. With the coefficient matrix and the orbital occupation number n one can construct the density matrix:

$$\begin{aligned} \mathbf{P}^{STO} &= \mathbf{C}n\mathbf{C}^T = \mathbf{\Delta}^{-1/2}\mathbf{\Delta}^{1/2}\mathbf{C}n\mathbf{C}^T\mathbf{\Delta}^{1/2}\mathbf{\Delta}^{-1/2} \\ &= \mathbf{\Delta}^{-1/2}\mathbf{D}n\mathbf{D}^T\mathbf{\Delta}^{-1/2} = \mathbf{\Delta}^{-1/2}\mathbf{P}^{LTO}\mathbf{\Delta}^{-1/2}, \end{aligned} \tag{3.22}$$

i.e.,

$$\mathbf{P}^{LTO} = \mathbf{\Delta}^{1/2}\mathbf{P}^{STO}\mathbf{\Delta}^{1/2}. \tag{3.23}$$

The density matrix is then used for calculating the Coulomb integrals:

$$\begin{aligned} J_{\mu\mu} &= \sum_{\sigma\lambda} P_{\sigma\lambda}^{STO}\langle\sigma^s\mu^s|\lambda^s\mu^s\rangle \\ &= \sum_{\sigma\lambda}\sum_{ij} S_{\sigma i}{}^{-1/2} P_{ij}^{LTO} S_{j\lambda}{}^{-1/2}\langle\sigma^s\mu^s|\lambda^s\mu^s\rangle \\ &= \sum_{ij} P_{ij}^{LTO}\sum_{\sigma\lambda} S_{\sigma i}{}^{-1/2}\langle\sigma^s\mu^s|\lambda^s\mu^s\rangle S_{j\lambda}{}^{-1/2} \end{aligned}$$

$$= \sum_{ij} P_{ij}^{LTO} \langle i^l \mu^s | j^l \mu^s \rangle, \tag{3.24}$$

where the superscripts s and l stand for STO and LTO respectively. Indeed, the Coulomb integrals in Slater type orbitals can be replaced by half-transformed integrals as the types shown in Eqn. 3.24 together with the Löwdin density matrix. Furthermore, we introduce the approximation

$$J_{\mu\mu} = \sum_{ij} P_{ij}^{LTO} \langle i^l \mu^s | j^l \mu^s \rangle \approx \sum_{ij} P_{ij}^{LTO} \langle i^l \mu^l | j^l \mu^l \rangle \tag{3.25}$$

$$\approx [\sum_{i_A j_A} P_{ij}^{LTO} \langle i_A \mu_A | j_A \mu_A \rangle + \sum_{i_{B \neq A}} P_{ii}^{LTO} \langle i_B \mu_A | i_B \mu_A \rangle] \text{ (INDO)}. \tag{3.26}$$

Based on the fact that after the half-transformation, the sum of one-center integrals tends to increase and the sum of two-center integrals decreases, leaving the total sum approximately unchanged [55]. Eqn. (3.25) says that the mixed STO-LTO integrals can be evaluated over LTO alone, as is traditionally done in ZDO methods. The conclusion that the two-electron Hamiltonian does not change much after the basis transformation is in agreement with this observation.

In the INDO/S parameterization, these integrals are, in fact, semiempirical Slater-Condon parameters [56] and γ_{AB} as in Eqn. (2.107). In XINDO, the one-center Coulomb matrix elements are evaluated the same way as they are done in INDO/S, except the Ohno-Klopman formula instead of the Mataga-Nishimoto formula is used for γ_{AB}.

The NDDO method has non-zero two-center Coulomb terms $\langle \mu_A \sigma_B | \nu_A \lambda_B \rangle$, and such integrals appear to be beneficial in the calculations of geometries. Incorporating these integrals can be done without the efforts of evaluating the extra two-center two-electron integrals. By applying the Mulliken approximation with the corresponding one-center two-electron integrals, $\bar{J}_{\mu\mu}$, defined as the following:

$$\bar{J}_{\mu\mu} \equiv \sum_{\lambda} P_{\lambda\lambda}^{LTO} \langle \lambda\mu | \lambda\mu \rangle, \tag{3.27}$$

which is similar to Eqn. (3.25) but only spherically symmetric integrals are included in $\bar{J}_{\mu\mu}$ and this types of integrals will be used to construct the two-center Coulomb integral $J_{\mu_A\sigma_B}$ and still maintain the rotational invariance.

Then the two-center Coulomb integrals can be calculated according to:

$$J_{\mu_A\sigma_B} = \frac{S_{\mu_A\sigma_B}}{2}(\bar{J}_{\mu_A\mu_A} + \bar{J}_{\sigma_B\sigma_B}). \tag{3.28}$$

Although Eqn. (3.28) is the expression for the two-center two-electron integrals, it contains not only the two-center terms. If one observes the expression of $\bar{J}_{\mu_A\mu_A}$, which contains contributions from two types of integrals: $\langle \mu_A\nu_A | \mu_A\nu_A \rangle$, and $\langle \mu_A\sigma_B | \mu_A\sigma_B \rangle$, where center B is any atomic center except A. Hence $J_{\mu_A\sigma_B}$ may contain three- and four-center contributions. The inclusion of such integrals is consistent with the treatment for the one-electron part of the off-diagonal elements. Errors in the Mulliken approximation here should cancel against similar errors in the one-electron matrix.

Exchange integrals

Due to the ZDO approximation, the only exchange integrals for which the half-transformation can be applied are $\langle \mu\nu | \mu\nu \rangle$, where both ϕ_μ and ϕ_ν are on center A.

Such type of integrals are of the same form as the Coulomb integrals. However, in general the half-transformation cannot be applied to the following type of exchange integrals,

$$K_{\mu_A \sigma_B} = \sum_{\nu\lambda} P_{\nu\lambda}^{LTO} \langle \mu_A \nu | \lambda \sigma_B \rangle. \tag{3.29}$$

To illustrate this, we have orbital ϕ_μ on atom A and ϕ_σ on atom B, and if we apply the half transformation from STO to LTO to exchange integrals,

$$K_{\mu_A \sigma_B} = \sum_{\nu\lambda} P_{\nu\lambda}^{STO} \langle \mu^s \nu^s | \lambda^s \sigma^s \rangle = \sum_{\nu\lambda} P_{\nu\lambda}^{LTO} \langle \mu^s \nu^l | \lambda^l \sigma^s \rangle, \tag{3.30}$$

then it becomes clear what the problem is: only one of the two orbitals with the same electronic coordinate is transformed, and one can not apply the ZDO approximation over such term $\phi_\mu^{s*} \phi_\lambda^l$. Therefore, Eqn. (3.30) offers no further simplification. We, then, keep the exchange integrals the same as in the INDO methods without further approximation since two-electron integrals change little between STOs and LTOs [50]. It is possible that when applying the Mulliken approximation to the two-center Coulomb integrals, at the same time, the two-center exchange integrals are approximated the same way by the corresponding one-center terms, and with an assumption that the one-electron correction parameters can take care of this error in an average manner.

The nuclear-nuclear repulsion

In order to obtain the total energy, a nuclear-nuclear repulsion expression compatible with the electronic part of the Hamiltonian is needed. The choice of this expression also has the influence over the geometry optimization calculations. In our formalism, the asymptotics of core-electron interaction when $R \to 0$ (one-center), γ', is much smaller than the Coulomb repulsion $1/R \to \infty$. If we adopt the value of $1/R$ for the nuclear-nuclear repulaion, the repulsion within the molecule will be too large in comparison with the attractive interaction. Therefore, a natural choice is to use the parameters for one-center core-electron attractions accompanied with the Ohno-Klopman formula for nuclear-nuclear repulsion

$$E_{nucl-nucl} = \sum_{A>B} \frac{Z_A^* Z_B^*}{((\frac{1}{(\gamma'_{\mu_A})_{avg}})^2 + R_{AB}^2)^{1/2}}. \tag{3.31}$$

A comparison between the theoretical repulsion integral and the semiempirical value is shown in Fig. (2.1).

3.2.3 Details of the Parameterization

In this section, the integrals that are used in XINDO are collected.

Diagonal one-electron

$$H_{\mu_A \mu_A} = U_{\mu_A \mu_A} + \sum_{B \neq A} V_{AB} + ECP, \tag{3.32}$$

where $U_{\mu\mu}$ is the atomic core integral and the one center ECP. The atomic core integral is determined from the average experimental energies of neutral atomic configurations. It contains the one-center kinetic energy and the one-center electron-nuclear attraction and the one-center ECP by construction. The expressions for core integrals of the first two rows of atoms are given by Karlsson and Zerner [57]:

$$\begin{aligned}
U_{ss} &= -I_s \text{ for H,} \\
U_{ss} &= -I_s;\ U_{pp} = -I_p \text{ for Li,} \\
U_{ss} &= -I_s - F^0(ss) \text{ for Be,} \\
U_{ss} &= -I_s - (Z^* - 1)F^0(ss) - \frac{(Z^* - 2)}{6}G^1(sp) \text{ for B-F,} \\
U_{pp} &= -I_s - (Z^* - 1)F^0(ss) - \frac{2(Z^* - 3)}{25}F^2(pp) + \frac{1}{3}G^1(sp) \text{ for B-F,} \quad (3.33)
\end{aligned}$$

where F^k and G^k are the semiempirical Slater-Condon factors [56], and Z^* is the effective core charge, and I_k is the ionization potential of the electron from orbital ϕ_k. The second term in Eqn. (3.32) includes the attraction between nucleus B and the electron on A, and the repulsion between the core electrons on B and the electron on A. In XINDO this term is expressed using the Ohno-Klopman formula Eqn. (3.14) with the parameters γ'_{μ_A} and γ'_{σ_B}, and Eqn. (3.16).

Off-diagonal one-electron

$$\begin{aligned}
H_{\mu_A\sigma_B} &= \langle\mu_A| - \frac{1}{2}\nabla^2 - V_A - V_B - \sum_{C\neq A,B} V_C|\sigma_B\rangle \\
&= t_{\mu_A\sigma_B} - \langle\mu_A|V_A|\sigma_B\rangle - \langle\mu_A|V_B|\sigma_B\rangle \\
&- \sum_{C\neq A,B} \langle\mu_A|V_C|\sigma_B\rangle + (ECP)_{\mu_A\sigma_B} + \beta b_{\mu_A\sigma_B}, \quad (3.34)
\end{aligned}$$

where $t_{\mu_A\sigma_B}$ is a kinetic energy element, evaluated *ab initio*. The integrals $\langle\mu_A|V_A|\sigma_B\rangle$ are also evaluated *ab initio*, but scaled to be compatible with the parameter γ'_{μ_A}. The three-center integrals $\langle\mu_A|V_C|\sigma_B\rangle$ are evaluated by Eqn. (3.18).

The last term in Eqn. (3.34), $\beta b_{\mu_A\sigma_B}$, is a correction term which is introduced to take care of the errors arising from the Mulliken approximation, unmodified exchange integrals, imperfect STO Hamiltonian, etc.. The Wolfsberg-Helmholtz formula is used:

$$\beta b_{\mu_A\sigma_B} = \frac{S_{\mu_A\sigma_B}}{2}(\beta b_{\mu_A} + \beta b_{\sigma_B}), \tag{3.35}$$

where βb_{μ_A} is an orbital dependent atomic parameter.

For two different spin orbitals ϕ_μ and ϕ_ν both located on center A, the one-electron integrals contain nothing but the ECP under the INDO approximation:

$$H_{\mu_A\nu_A} = -\sum_{\alpha_{B_{(core)}}\neq A} S_{\mu_A\alpha_B}\varepsilon_{\alpha_B}S_{\alpha_B\nu_A}. \tag{3.36}$$

Diagonal two-electron

For a closed-shell system,

$$G^{STO}_{\mu_A\mu_A} \approx \sum_{\lambda_A\sigma_A} P^{LTO}_{\lambda\sigma}[\langle\mu_A\lambda_A|\mu_A\sigma_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\sigma_A\mu_A\rangle] + \sum_{B\neq A} P^{LTO}_{BB}\gamma_{AB}. \tag{3.37}$$

The values of $\langle\mu_A\lambda_A|\mu_A\sigma_A\rangle$ and $\langle\mu_A\lambda_A|\sigma_A\mu_A\rangle$ are determined by the corresponding semiempirical Slater-Condon factors [56]. γ_{AB} is evaluated by the Ohno-Klopman formula Eqn. (3.14) and INDO/S one-center Coulomb integral γ_{μ_A}:

$$\gamma_{\mu_A} = I_{\mu_A} - A_{\mu_A}, \tag{3.38}$$

where I_{μ_A} is the ionization potential and A_{μ_A} is the electron affinity of atomic orbital ϕ_{μ_A}.

Off-diagonal two-electron

In this catagory there are two types of two-electron integrals, $G_{\mu_A\nu_A}$ and $G_{\mu_A\sigma_B}$.

$$G^{STO}_{\mu_A\nu_A} \approx \frac{1}{2}P^{LTO}_{\mu_A\nu_A}[3\langle\mu_A\nu_A|\nu_A\mu_A\rangle - \langle\mu_A\nu_A|\mu_A\nu_A\rangle]; \tag{3.39}$$

$$G^{STO}_{\mu_A\sigma_B} \approx \frac{S_{\mu_A\sigma_B}}{2}(\bar{J}_{\mu_A\mu_A} + \bar{J}_{\sigma_B\sigma_B}) - \frac{1}{2}P^{LTO}_{\mu_A\sigma_B}\gamma_{AB}. \tag{3.40}$$

There are different suggestions [55] concerning the form of the overlap elements in the Mulliken approximation. The original formula by Mulliken [44], which is the orbital overlap, is used in evaluating both one- and two-electron integrals in the XINDO method.

SCF procedure of XINDO

In the previous section we have introduced all the terms present in the XINDO model Hamiltonian. For a closed-shell system of s- and p-orbitals,

$$F^{STO}_{\mu_A\mu_A} = U_{\mu_A\mu_A} - \sum_{\sigma_B\neq A} n_{\sigma_B}\gamma'_{\mu_A\sigma_B} - \sum_{\alpha_{B(core)}\neq A} S_{\mu_A\alpha_B}\varepsilon_{\alpha_B}S_{\alpha_B\mu_A}$$

$$
\begin{aligned}
&+ \sum_{\lambda_A \lambda_A} P_{\lambda\lambda}^{LTO}[\langle \mu_A \lambda_A | \mu_A \lambda_A \rangle - \frac{1}{2} \langle \mu_A \lambda_A | \lambda_A \mu_A \rangle] \\
&+ \sum_{B \neq A} P_{BB}^{LTO} \gamma_{AB}, \qquad (3.41) \\
F_{\mu_A \nu_A}^{STO} &= - \sum_{\alpha_{B_{(core)}} \neq A} S_{\mu_A \alpha_B} \varepsilon_{\alpha_B} S_{\alpha_B \nu_A} + \frac{1}{2} P_{\mu_A \nu_A}^{LTO} [3 \langle \mu_A \nu_A | \nu_A \mu_A \rangle \\
&- \langle \mu_A \nu_A | \mu_A \nu_A \rangle], \qquad (3.42) \\
F_{\mu_A \sigma_B}^{STO} &= t_{\mu_A \sigma_B} - \langle \mu_A | V_A | \sigma_B \rangle - \langle \mu_A | V_B | \sigma_B \rangle - \sum_{C \neq A,B} \frac{S_{\mu_A \sigma_B}}{2} (\langle \mu_A | V_C | \mu_A \rangle \\
&+ \langle \sigma_B | V_C | \sigma_B \rangle) - \sum_{\alpha_{C_{(core)}}} S_{\mu_A \alpha_C} \varepsilon_{\alpha_C} S_{\alpha_C \sigma_B} + \frac{S_{\mu_A \sigma_B}}{2} (\bar{J}_{\mu_A \mu_A} + \bar{J}_{\sigma_B \sigma_B}) \\
&- \frac{1}{2} P_{\mu_A \sigma_B}^{LTO} \gamma_{AB} + \beta b_{\mu_A \sigma_B}, \qquad (3.43)
\end{aligned}
$$

Most of the changes are made for the off-diagonal elements of the Fock matrix, and this is clear if one compares Eqn. (3.43) with Eqn. (2.71). Table 3.1 and Table 3.2 contain the Fock matrix elements of the XINDO and INDO/S methods.

Table 3.1. Fock matrix elements of the XINDO methods, in (s,p) basis set

$F_{\mu_A\mu_A}$	$\langle\mu_A\vert-\frac{1}{2}\nabla^2-V_A\vert\mu_A\rangle$	$U_{\mu_A\mu_A}$
	$\sum_{B\neq A}\langle\mu_A\vert V_B\vert\mu_A\rangle$	$\sum_{\sigma_B}n_{\sigma_B}\gamma'_{\mu_A\sigma_B}$+ECP
	Two-electron	$P_{AA}[\langle\mu_A\lambda_A\vert\mu_A\lambda_A\rangle-\frac{1}{2}\langle\mu_A\lambda_A\vert\lambda_A\mu_A\rangle]$ $+\sum_{B\neq A}P_{BB}\gamma_{AB}$
$F_{\mu_A\nu_A}$	$\langle\mu_A\vert-\frac{1}{2}\nabla^2-V_A\vert\nu_A\rangle$	0.0
	$\sum_{B\neq A}\langle\mu_A\vert V_B\vert\nu_A\rangle$	ECP
	Two-electron	$\frac{1}{2}P_{\mu_A\nu_A}[3\langle\mu_A\nu_A\vert\nu_A\mu_A\rangle-\langle\mu_A\nu_A\vert\mu_A\nu_A\rangle]$
$F_{\mu_A\sigma_B}$	$\langle\mu_A\vert-\frac{1}{2}\nabla^2\vert\sigma_B\rangle$	*ab initio*
	$\langle\mu_A\vert-V_A-V_B\vert\sigma_B\rangle$	*ab initio*
	$-\sum_{C\neq A,B}\langle\mu_A\vert V_C\vert\sigma_B\rangle$	$-\frac{S_{\mu_A\sigma_B}}{2}\sum_{\lambda_C}n_{\lambda_C}[\gamma'_{\mu_A\lambda_C}+\gamma'_{\sigma_B\lambda_C}]$ +ECP
	Two-electron	$\frac{S_{\mu_A\sigma_B}}{2}[\bar{J}_{\mu_A\mu_A}+\bar{J}_{\sigma_B\sigma_B}]-\frac{1}{2}P_{\mu_A\sigma_B}\gamma_{AB}$
	correction	$\frac{S_{\mu_A\sigma_B}}{2}[\beta b_{\mu_A}+\beta b_{\sigma_B}]$

Table 3.2. Fock matrix elements of the INDO/S method, in (s,p) basis set

$F_{\mu_A\mu_A}$	$\langle\mu_A\| -\frac{1}{2}\nabla^2 - V_A\|\mu_A\rangle$	$U_{\mu_A\mu_A}$
	$\sum_{B\neq A}\langle\mu_A\|V_B\|\mu_A\rangle$	$\sum_{B\neq A} Z_B^* \gamma_{AB}$
	Two-electron	$P_{AA}[\langle\mu_A\lambda_A\|\mu_A\lambda_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A\|\lambda_A\mu_A\rangle]$ $+\sum_{B\neq A} P_{BB}\gamma_{AB}$
$F_{\mu_A\nu_A}$	$\langle\mu_A\| -\frac{1}{2}\nabla^2 - V_A\|\nu_A\rangle$	0.0
	$\sum_{B\neq A}\langle\mu_A\|V_B\|\nu_A\rangle$	0.0
	Two-electron	$\frac{1}{2}P_{\mu_A\nu_A}[3\langle\mu_A\nu_A\|\nu_A\mu_A\rangle - \langle\mu_A\nu_A\|\mu_A\nu_A\rangle]$
$F_{\mu_A\sigma_B}$	$\langle\mu_A\| -\frac{1}{2}\nabla^2\|\sigma_B\rangle$	
	$\langle\mu_A\| - V_A - V_B\|\sigma_B\rangle$	$\frac{S_{\mu_A\sigma_B}}{2}[\beta_A + \beta_B]$
	$-\sum_{C\neq A,B}\langle\mu_A\|V_C\|\sigma_B\rangle$	
	Two-electron	$-\frac{1}{2}P_{\mu_A\sigma_B}\gamma_{AB}$

Semiempirical methods of the ZDO type assume an identity overlap matrix in the process of diagonalizing the Fock matrix and this is justified by considering the Hamiltonian transformed to the orthogonalized atomic basis set. However, traditional ZDO methods may not have all the terms for the orthogonalized basis set included in the model Hamiltonian and that causes difficulty in applying the ZDO methods for general purposes. Jug, Thiel and many others have tried to modify the ZDO methods by adding correction terms into the Hamiltonian in the LTO representation. The XINDO method, on the other hand, constructs the Hamiltonian in the STO representation, similar to the EHT in this sense, but, of course, unlike EHT, our new method contains not only one-electron but also two-electron integrals.

In XINDO, the Hamiltonian is built over a non-orthogonal basis set and yet keeps the evaluation of integrals to a minimum. The density matrix used for building the two-electron part of the Fock matrix is still the Löwdin type density matrix as illustrated in Eqn. (3.24). The Roothaan equation (Eqn. (2.18)) is solved with non-identity overlap matrix. The orbital energies are obtained from the solutions of the Roothaan equation, and so are the corresponding molecular orbitals, and thence the density matrix which corresponds to the STO. Total energy is evaluated based on the STO density as the Fock matrix is created over the STO basis.

$$E_{total} = \frac{1}{2}\sum_{\mu\nu} P_{\mu\nu}^{STO}(H_{\mu\nu} + F_{\mu\nu}) + \sum_{A>B} \frac{Z_A^* Z_B^*}{((\frac{1}{\gamma_{\mu_A}})_{avg}^2 + R_{AB}^2)^{1/2}}. \tag{3.44}$$

Here the nuclear-nuclear repulsion energy is evaluated using the parameters for electron-nuclear attraction.

In such an arrangement, we include the overlap, in spirit, into the XINDO Hamiltonian. This results not only in the improvement of the description of the antibonding orbitals, but also, through the diagonalization procedure, multi-center interactions are included. Hence this treatment may benefit the calaulations related to, e.g., molecular geometries, multipole interactions, rotational barriers, etc..

We then, back transform the density matrix to the Löwdin type density to build the two-electron matrix and proceed the next iteration until the STO density from two consecutive SCF cycles differ less than a given tolerance.

3.2.4 Similar Work in the Field

Different proposals for a multi-purposed semiempirical method have been presented by others groups and indeed there has been some successful attempts. As mentioned in the previous section most of the them tried to improve the ZDO Hamiltonian in the LTO representation. This is one of the main differences between XINDO and the other methods.

It may be worthwhile to discuss the problems that possibly exist in the current ZDO methods. These problems are related to the effects to the Hamiltonian arising from the basis set orthogonalization transformation. As mentioned, it has been shown numerically by Coffey [51] that in the case of the C_2 molecule, the contributions from the effective core potential (ECP) together with the orthogonalization corrections, are about equal in magnitude to the penetration integrals, $Z_B^*\gamma_{AB} - V_{AB}$, which has been stated in the review chapters (see Eqn. (2.59), (2.60), and (2.61)). However, the integrals used by Coffey were all theoretically evaluated using STOs, and contain no electron correlation. Such integrals are ideal for geometry optimization but not for calculating spectroscopic properties. There is no reason for Coffey's argument to hold when using other types of integrals, e.g., the two-electron integrals in the INDO/S method. Furthermore, a two-center situation is far easier to handle than systems with three or more atoms.

Many other studies have been presented concerning the orthogonalization correction [30, 46, 49–51, 58–68]. The recent conclusion from these studies is that the orthogonalization correction should be included, and therefore the ECP should be taken into consideration explicitly as well. Jug *et al.* has presented a semiempirical Hamiltonian [30] which is a model at the INDO level. The ECP is added into their one-electron Hamiltonian, and the orthogonalization correction term is obtained by doing a Taylor expansion of the overlap matrix $\mathbf{\Delta}^{-1/2}$ (Eqn. (3.12)), and collecting terms up to the second order in $\mathbf{S}$. Similar work has been done at the NDDO level by Thiel *et al.* [50, 67]. It turns out that both the ECP and the orthogonalization correction term are repulsive so that the consitituent atomic orbitals are raised energetically. However they are still subject to a symmetric splitting between bonding and antibonding molecular orbitals. They chose the parameters properly so that the energy of the bonding molecular orbital is close to the ionization potential (Koopmans' theorem), which also result in an energy lift for the antibonding molecular orbital. The energy of the antibonding MO has been underestimated by all current semiempirical methods. It has also been reported that in the new NDDO model, three-center interactions are included from terms that originate from the overlap expansion. This makes the prediction of molecular conformations somewhat better. However, there are still no calculations of electronic spectra reported using these models.

The differences between XINDO and the latest ZDO models by Jug [68] at the INDO level or by Thiel [50] at the NDDO level are summerized in Table 3.3.

Table 3.3. Comparison between the XINDO Hamiltonian and the orthogonalization-corrected Hamiltonian by Jug *et al.* [68] or Thiel *et al.* [50]

Feature	Orthogonalization corrected	XINDO
Basis set	LTO	$\approx$ STO
Multi-center effect	≤ 3	> 4
Penetration integral	from expanding the overlap series	from assigning γ' parameter
Possible flaw	overlap series may not converge	parameter needs to be further improved
Two-electron integrals	*ab initio*	data from fitting atomic spectra

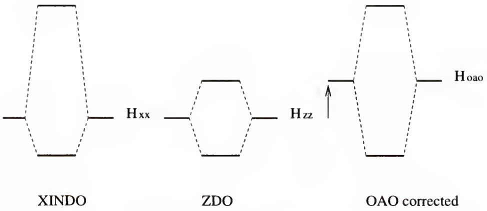

Figure 3.1. MO schemes for XINDO, ZDO, and orthogonalization corrected methods

The MO schemes in Fig. 3.1 are constructed from the one-electron matrix elements. H_{xx} denotes the XINDO elements and the resulting MOs split unsymmetrically. H_{zz} (which is similar in magnitude with H_{xx}, i.e., $H_{zz} \approx H_{xx}$) denotes the one-electron matrix element in ZDO methods, and H_{oao} stands for the matrix element which is corrected with the atomic orbital orthogonalization effect. The latter two types of methods yield symmetrically split MOs, but the repulsive effect from the orbital orthogonalization correction raises the H_{oao}, which results in the higher energy for the antibonding MO compared to standard ZDO. The reason why the XINDO method gives an unsymmetric split was discussed in Eqn. (3.2): a result of including the overlap into the model.

Prior to this thesis some efforts were made to build a new Hamiltonian within INDO/S scheme by reformulating the functional form of the resonance integrals β

[69, 70]:

$$\beta_{\mu_A \sigma_B} = r^m \exp[-(\alpha_{\mu_A} + \alpha_{\sigma_B}) r^2] (\frac{\beta_{\mu_A} + \beta_{\sigma_B}}{2}), \tag{3.45}$$

where r is the interatomic distance, m, α, and β are parameters in the model to be adjusted to obtain a better distance dependence of the resonance integrals. The equation above comes from the understanding that the distance dependences of $H^{STO}_{\mu_A \sigma_B}$ and $H^{LTO}_{\mu_A \sigma_B}$ are different. Since

$$H^{STO}_{\mu_A \sigma_B} \propto S_{\mu_A \sigma_B}, \tag{3.46}$$

and according to Eqn. (3.9),

$$H^{LTO}_{\mu_A \sigma_B} \propto S_{\mu_A \sigma_B} / (1 - S^2_{\mu_A \sigma_B}). \tag{3.47}$$

Therefore simple forms such as the Wolfsberg-Helmholtz formula [23] may not be sufficient for LTO off-diagonal one-electron matrix elements.

This model, Eqn. (3.45), accurately reproduces electronic excitations because the parameterization scheme is exactly the same as in the INDO/S method with the exception, of course, of the resonance integrals. It is able to perform molecular geometry calculation [70] to some extent. However, multi-center terms are still not present, thus we suspect the calculation of geometry may be limited in accuracy.

CHAPTER 4
PARAMETERS AND OTHER RESULTS

4.1 Parameters

All the parameters in this method are chosen as orbital dependent atomic parameters. Two-center bonding parameters are avoided because it is a complicated work to select a parameterization set with the capability to represent all sorts of bonding situations for different molecules that contain similar atom pairs.

We want this model to have correct asymptotic limit as the inter-nuclear distances become large. To do so, we may again consider a homonuclear diatomic molecule with bond length infinitely long, and the energy expression of this system is simplified to

$$E_{R\to\infty} = Z_A^2\left(\frac{1}{[(\frac{1}{(\gamma_A')_{avg}})^2 + R_\infty^2]^{1/2}} - 2\frac{1}{[(\frac{1}{(\gamma_A')_{avg}})^2 + R_\infty^2]^{1/2}} + \frac{1}{[(\frac{1}{(\gamma_A)_{avg}})^2 + R_\infty^2]^{1/2}}\right), \tag{4.1}$$

where the first term is the nuclear-nuclear repulsion, the second term is the electron-nuclear attraction, and the last term is the electron-electron repulsion. $(\gamma_A')_{avg}$ is the nuclear-electron attraction parameter in XINDO, and here an average value taken from all orbitals in the atom. Similarly the $(\gamma_A)_{avg}$ is an average value of all the one-center two-electron integrals. It is clear from this energy expression that at infinite distance, the binding energy becomes zero. We also want the potential curve of this system to approach zero with positive slope asympotically ($\partial E_\infty / \partial R \geq 0$), so we differentiate Eqn. (4.1) with respect to the inter-nuclear distance R:

$$\frac{\partial E_{R\to\infty}}{\partial R} = Z_A^2(2R)(\frac{-1}{2})(\frac{-1}{[(\frac{1}{(\gamma_A^{'})_{avg}})^2 + R^2]^{3/2}} + \frac{1}{[(\frac{1}{(\gamma_A)_{avg}})^2 + R^2]^{3/2}}) \geq 0, \qquad (4.2)$$

from which we obtain

$$\frac{1}{[(\frac{1}{(\gamma_A^{'})_{avg}})^2 + R^2]^{3/2}} \geq \frac{1}{[(\frac{1}{(\gamma_A)_{avg}})^2 + R^2]^{3/2}} \qquad (4.3)$$

so we may deduce the following relation

$$(\gamma_A^{'})_{avg} \geq (\gamma_A)_{avg}. \qquad (4.4)$$

From this we know that the parameters for nuclear-electron attraction should be larger than the one-center two-electron integrals in average to give the XINDO method a correct asymptotic behavior. This is certainly so in *ab initio* methods, for example, where $\gamma_A = 0.3633\xi$ and $\gamma_A^{'} = 0.5\xi$ (ξ is the exponent of a Slater type orbital).

Hence, based on Eqn. (4.4) we start to search for the parameters by calculating the homonuclear diatomic molecules: H_2, C_2, N_2, O_2. Before knowing the precise ranges of the parameters, we do XINDO calculations on these molecules by trial and error. For each of the diatomic molecules, we first guess the $\gamma_s^{'}$, $\gamma_p^{'}$, βb_s, and

βb_p parameters for each atom (except H_2, where only s-parameters are applied). When the calculated ionization potentials are approximately correct, and the highest occupied molecular orbitals have the correct symmetries, we then proceed with the geometry calculations with the same parameters. If the calculated bond length is close to the experimental value from the literature, then the set of parameters for this atom can be accepted as a good initial guess.

The next step is to tune the parameters even further using medium-sized molecules. A set of molecules are used for geometry optimizations using the XINDO method. By the aid of the simplex algorithm [71–73] we can minimize the deviation between the calculated results and the expected values and finally the parameters corresponding to the smallest error (locally) are obtained.

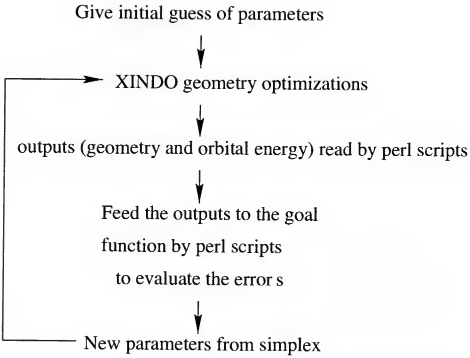
Give initial guess of parameters
XINDO geometry optimizations
outputs (geometry and orbital energy) read by perl scripts
Feed the outputs to the goal
function by perl scripts
to evaluate the error s
New parameters from simplex

Figure 4.1. The flowchart of the procedure of obtaining XINDO parameters

Fig. 4.1 summerizes the prodecdure that is used to obtain the C, H, N, and O parameters for the XINDO method. The more molecules included in the training set the better parameters may be obtained. Currently the training set contains the following molecules: methane, ethane, ethene, ethyne, benzene, naphthalene, pyridine, pyrazine, pyrrole, imidazole, methylamine, ammonia, water, phenol, p-benzoquinone, furan, propionic acid, ether, methanol, and acetaldehyde.

The properties that we use as the criteria for XINDO calculations are the highest few orbital energies, and the molecular structures. Good parameters can have the orbital energies close to the experimental ionization potential (Koopmans' theorem), and the calculated molecular structures similar to the experimental geometries.

We also examine the parameters for different sizes of molecules to ensure that there are not any parts in the Hamiltonian that introduce errors that accumulate as the molecular size increases. Such "size inconsistency" would cause problems when the model is applied to cases with different ranges of size other than the size of molecules in the training set. It turns out that no problem of this nature exists, and the errors among various sizes of hydrocarbons are found similar.

The parameters which are currently used in the XINDO model are shown in Table 4.1. At this stage, we have managed to obtain the parameters for H, C, N, and O, which are the elements that constitute most organic molecules. The parameters should be further refined and therefore they are called "estimated" for the time being.

Table 4.1. Estimated parameters (in eV) for the XINDO model

Atom	$\langle s_A \vert V_A \vert s_A\rangle \equiv \gamma'_{A_s}$	$\langle p_A \vert V_A \vert p_A\rangle \equiv \gamma'_{A_p}$	βb_s	βb_p
H	13.4170		-37.6957	
C	17.4366	11.1128	-42.3887	-52.6009
N	18.2931	11.61	-51.6516	-64.7970
O	17.6873	12.7703	-62.5875	-97.8456

The parameters of one-center two-electron integrals γ_A in the INDO/S method are shown in Table 4.2.

Table 4.2. γ_A parameters (in eV) in the INDO/S method (for Ohno-Klopman formula)

Atom	H	C (both s and p)	N (both s and p)	O (both s and p)
γ_A	12.85	11.11	12.01	13.0

It is clear from Table 4.1 and Table 4.2 that the parameters used in the XINDO method fulfill the relation in Eqn. (4.4).

4.2 Test Cases

4.2.1 Geometry Optimization

To check the performance of the model and the parameters, several examples are calculated and illustrated in the following. First of all, the ability to optimize molecular geometry is the primary goal to achieve in the XINDO model. Therefore, some geometry optimization outputs are reported in Table 4.3.

The calculated results seem fairly good although there is still plenty of room for improvement as said earlier.

Table 4.3. Optimized geometries with the XINDO method

Molecule	Property	This work	Experimental
ethane	C-C	1.595 Å	1.536 Å [74]
	C-H	1.182 Å	1.102 Å [74]
ethene	C=C	1.316 Å	1.339 Å [75]
	C-H	1.145 Å	1.085 Å [75]
ethyne	C≡C	1.132 Å	1.203 Å [76]
	C-H	0.997 Å	1.062 Å [76]
benzene	C-C	1.395 Å	1.397 Å [77]
	C-H	1.093 Å	1.084 Å [77]
naphthalene	C-C	1.392 Å	1.410 Å [78]
	C-C	1.408 Å	1.425 Å [78]
	C-C	1.360 Å	1.361 Å [78]
	C-C	1.429 Å	1.420 Å [78]
	C-H	1.065 Å	1.07 Å [78]
pyridine	C-N	1.328 Å	1.338 Å [79]
	C-C	1.398 Å	1.394 Å [79]
p-benzoquinone	C=O	1.246 Å	1.222 Å [80]
	C-C	1.469 Å	1.477 Å [80]
	C=C	1.347 Å	1.322 Å [80]

4.2.2 $C_3H_3^+$

We examine the isomers of $C_3H_3^+$ to demonstrate the conformal properties calculated by XINDO. The INDO methods are known to exaggerate the stabilization of ring conformers. The lack of three-center integrals might be reponsible for some of this problem since in that case, the INDO methods cannot properly describe such interactions.

However, the ring form of $C_3H_3^+$ is anyway predicted to be more stable but energetically it is only 1.08 eV (25 Kcal/mol) [81] lower than the linear conformer. The INDO method tends to overestimate the energy difference between these two conformers because of the tendency of the INDO methods to form rings.

Table 4.4. Relative energies (in eV) of $C_3H_3^+$ conformers from different methods

$C_3H_3^+$ conformer	AM1	INDO/S	INDO/1	XINDO	Exp [81]
C_{2v} (Linear)	0.0	0.0	0.0	0.0	0.0
D_{3h} (Ring)	0.063	-7.967	-6.357	-2.711	-1.08

Although XINDO still overestimates the stabilization of the D_{3h} conformer, there is an obvious improvement over the INDO methods.

4.2.3 O_3

There exist two conformers of the ozone molecule, O_3 at the Hartree-Fock level of theory, bent or equallateral triangle. The electronic configuration of ozone can be described by three valence bond structures, consequently, the one-determinant description of the SCF level calculations is not able to give the correct electronic structure with only one minimum at 117°. Semiempirical methods bring some electron correlation into systems of interest, but ozone has inherently a two-configuration ground state.

The multi-center terms included in the XINDO Hamiltonian and the electron correlation that the model obtains from imitating the experimental data yield an optimized O_3 structure that seems very good.

Table 4.5. Optimized O_3 geometry

O_3 conformer	AM1	INDO/1	XINDO	Exp [82]
O-O	1.1604 Å	1.1438 Å	1.261 Å	1.278 Å
<OOO	121.04°	123.02°	110.5°	116.8°

CHAPTER 5
CONCLUDING REMARK

The addition of penetration integrals (expression (2.60)) has made it possible to obtain good molecular geometries by using the semiempirical two-electron integrals, which are conventionally used only for calculating spectra. When calculating the geometries without the ECP, the bond lengths tend to be too short in comparison with the experimental values. Such results are expected when the penetration integrals are applied, as pointed out by Pople [20]. However, with the ECP added to the one-electron part of the Hamiltonian, the calculated bond lengths are much improved.

The current parameters for C and O yield the dipole moment of the CO molecule 0.1712 Debye pointing towards the carbon atom (exp. 0.11 Debye [83]). This is an improvement in the calculated charge distribution compared to the INDO/S method. The same parameters for O also yield better O_3 geometry compared to INDO/1 and AM1 methods (see previous chapter). The geometry optimization of the staggered form of the ethane molecule by using XINDO gives the angle 109° on average (110° and 108°). The multi-center terms that are included in both off-diagonal one- and two-electron integrals results in a better angular description and also the charge distribution. Thus from the promising results so far, this method seems to have great potential. Even though there are some additional terms to be calculated now, most of them are one-electron integrals, and the integrals $J_{\mu_A\sigma_B}$ are evaluated by using the corresponding diagonal elements $J_{\mu_A\mu_A}$ and $J_{\sigma_B\sigma_B}$ according to Eqn. (3.28). Therefore, the evaluation of these new terms is not time consuming, compared with the time needed for the diagonalization procedure, which is the same as in the INDO/S method.

There are many further implementations to be done with the XINDO model. First of all, we will make the XINDO method able to perform calculations of molecular spectroscopic properties. The two-electron integrals that are used in the XINDO method are the same as in the INDO/S method. Therefore we expect that just by finishing the compatible CI program, the XINDO method should be able to give as good calculated spectra as does the INDO/S method. Then we may be able to calculate molecular geometries of excited states and generate excited states potential energy surfaces.

Up to now, the parameterization of the XINDO method is done for some of the first row elements. It is far from a complete model if it cannot be used to calculate transition metal systems. To do so, we need to formulate the Hamiltonian with proper expressions and parameters for a basis set including *s*-, *p*-, *d*- and *f*- functions.

And we should not forget that the XINDO method has the overlap incorporated. This allows us to develop a semiempirical method which is parameterized over an extended basis set. The different orbital exponents can be used to calculate different sets of the overlap integrals. By applying different parameters to each set of exponents, the method can benefit by the more flexible basis sets. Eventually it may become conceivable to calculate Rydberg state electronic excitations using extended basis set included in the XINDO method.

REFERENCES

[1] E. Schrödinger, Ann. Physik **79**, 361 (1926).

[2] M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

[3] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford University Press, Clarendon Press, Oxford, 1954.

[4] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 (1928).

[5] W. Pauli, Z. Physik **31**, 765 (1925).

[6] V. Fock, Z. Physik **61**, 126 (1930).

[7] J. C. Slater, Phys. Rev. **35**, 210 (1930).

[8] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[9] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

[10] G. G. Hall, Proc. Roy. Soc. London Ser. A **205**, 541 (1951).

[11] P.-O. Löwdin, Adv. Chem. Phys. **2**, 207 (1959).

[12] J. Linderberg and N. Y. Öhrn, *Propagators in Quantum Chemistry*, Academic Press, London, 1973.

[13] E. P. Hückel, Z. Physik **70**, 204 (1931).

[14] R. Hoffman, J. Chem. Phys. **39**, 1397 (1963).

[15] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466 (1953).

[16] J. A. Pople, Trans. Faraday Soc. **49**, 1375 (1953).

[17] R. G. Parr, J. Chem. Phys. **20**, 1499 (1952).

[18] R. Pariser, J. Chem. Phys. **21**, 568 (1953).

[19] J. A. Pople and G. A. Segal, J. Chem. Phys. **43**, S136 (1965).

[20] J. A. Pople and G. A. Segal, J. Chem. Phys. **44**, 3289 (1966).

[21] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, J. Chem. Phys. **47**, 2026 (1967).

[22] D. P. Santry and G. A. Segal, J. Chem. Phys. **47**, 158 (1967).

[23] M. Wolfsberg and L. Helmholtz, J. Chem. Phys. **20**, 837 (1962).

[24] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys **6**, 645 (1938).

[25] M. J. S. Dewar and W. Thiel, J. Amer. Chem. Soc. **99**, 4899 (1977).

[26] M. J. S. Dewar and W. Thiel, J. Amer. Chem. Soc. **99**, 4907 (1977).

[27] R. G. Parr, J. Chem. Phys. **33**, 1184 (1960).

[28] B. Voigt, Theor. Chim. Acta **31**, 289 (1973).

[29] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[30] D. N. Nanda and K. Jug, Theor. Chim. Acta **57**, 95 (1980).

[31] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra*, Cambridge University Press, Cambridge, 1935.

[32] J. C. Slater, *Quantum Theory of Atomic Structure*, McGraw Hill, New York, 1960.

[33] J. D. Bene and H. H. Jaffé, J. Chem. Phys. **48**, 1807, 4050 (1968).

[34] J. D. Bene and H. H. Jaffé, J. Chem. Phys. **49**, 122 (1968).

[35] J. D. Bene and H. H. Jaffé, J. Chem. Phys. **50**, 1126 (1969).

[36] K. Nishimoto and N. Mataga, Z. Physik. Chem. **12**, 335 (1957).

[37] J. Ridley and M. C. Zerner, Theor. Chim. Acta **32**, 111 (1973).

[38] J. Ridley and M. C. Zerner, Theor. Chim. Acta **42**, 223 (1976).

[39] M. C. Zerner, G. H. Loew, R. F. Kirchner, and U. T. Mueller-Westerhoff, J. Am. Chem. Soc. **102**, 589 (1980).

[40] M. J. S. Dewar, E. G. Zoebisch, E. F.Healy, and J. J. P. Stewart, J. Amer. Chem. Soc. **107**, 3902 (1985).

[41] J. J. P. Stewart, J. Comput. Chem. **10**, 209, 221 (1989).

[42] G. Náray-Szabó, P. R. Surján, and J. G. Ángyán, *Applied Quantum Chemistry*, D. Reidel Publishing Company, 1987.

[43] M. C. Zerner, Molecular Physics **23**, 963 (1972).

[44] R. S. Mulliken, J. Chim. Phys. **46**, 497, 675 (1949).

[45] P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).

[46] I. Fischer-Hjalmars, Adv. Quantum Chem. **2**, 25 (1965).

[47] J. N. Murrel and A. J. Harget, *Semi-empirical self-consistent-field molecular orbital theory of molecules*, Wiley-Interscience, 1972.

[48] W. Kutzelnigg, *Einfuhrung in die Theoretische Chemie*, volume 2, Verlag Chemis, Weinheim, 1978.

[49] I. Fischer-Hjalmars, J. Chem. Phys. **42**, 1962 (1965).

[50] W. Weber and W. Thiel, to be published.

[51] P. Coffey, Int. J. Quantum Chem. **VIII**, 263 (1974).

[52] K. Ohno, Theoret. Chim. Acta **2**, 219 (1964).

[53] G. Klopman, J. Amer. Chem. Soc. **86**, 4550 (1964).

[54] K. Siegbahn et al., *ESCA Applied to Free Molecules*, North-Holland, Amsterdam, 1969.

[55] M. C. Zerner, in *Approximate Methods for Large Molecules and Localized States in Solids*, edited by F. Herman, A. D. Mclean, and R. K. Nesbet, Plenum, New York-London, 1973.

[56] J. Hinze and H. H. Jaffe, J. Chem. Phys. **38**, 1834 (1963).

[57] G. Karlsson and M. C. Zerner, Int. J. Quantum Chem. **VII**, 35 (1973).

[58] R. D. Brown and K. R. Roby, Theor. Chim. Acta **16**, 175 (1970).

[59] K. R. Roby, Chem. Phys. Lett **11**, 6 (1971).

[60] K. R. Roby, Chem. Phys. Lett **12**, 579 (1972).

[61] G. S. Chandler and F. E. Grader, Theor. Chim. Acta **54**, 131 (1980).

[62] D. B. Cook, P. C. Hollis, and R. Mcweeny, Mol. Phys. **13**, 553 (1967).

[63] S. de Bruijn, Int. J. Quant. Chem. **25**, 367 (1984).

[64] J. Spanget-Larsen, Theor. Chim. Acta **55**, 165 (1980).

[65] P. Coffey and K. Jug, J. Am. Chem. Soc. **95**, 7575 (1973).

[66] K. Jug, R. Iffert, and J. Schulz, Int. J. Quant. Chem. **32**, 265 (1987).

[67] M. Kolb and W. Thiel, J. Comput. Chem. **14**, 775 (1993).

[68] B. Ahlswede and K. Jug, J. Comput. Chem. **20**, 563, 572 (1999).

[69] Y.-W. Hsiao, Oral presentation 1994.

[70] J. D. Da Motta Neto, New Parametric Scheme of the Resonance Integrals at INDO/1 approximation, Ph.D. dissertation, University of Florida, 1997.

[71] J. A. Nelder and R. Mead, Computer Journal **7**, 308 (1965).

[72] L. A. Yarbro and S. N. Deming, Analytica Chim Acta **73**, 391 (1974).

[73] S. L. S. Jacoby, J. S. Kowalik, and J. T. Pizzo, *Iterative Methods for Nonlinear Optimization Problems*, Prentice-Hall, Englewood Cliffs, NJ, 1972.

[74] G. E. Hansen and D. M. Dennison, J. Chem. Phys. **20**, 313 (1952).

[75] J. L. Duncan, I. J. Wright, and D. V. Lerberghe, J. Mol. Spectrosc. **42**, 463 (1972).

[76] A. Baldacci, S. Ghersetti, S. C. Hurlock, and K. N. Rao, J. Mol. Spectrosc. **59**, 116 (1976).

[77] A. Langseth and B. P. Stoicheff, Can. J. Phys. **34**, 350 (1956).

[78] C. P. Brock and J. D. Dunitz, Acta Crystallogr. B **38**, 2218 (1982).

[79] G. O. Sorensen and L. Mahler, J. Mol. Struct. **20**, 119 (1974).

[80] J. Trotter, Acta Crystallogr. **13**, 86 (1960).

[81] F. P. Lossing, Can. J. Chem. **50**, 3973 (1972).

[82] CRC Handbook of Chemistry and Physics, 72nd edition.

[83] K. H. Hellwege, *Numerical Data and Functional Relationships in Science and Technology, Group II*, volume 14, subvolume a, Springer-Verlag, Heidelberg, 1982.

BIOGRAPHICAL SKETCH

Ya-Wen Hsiao was born in 1967 in Taiwan. When she was around one year old, her father moved to Taipei for another teaching job, so she also moved there. Because of the unfortunate death of her mother at the end of her first school year, Ya-Wen and her younger sister went to southern Taiwan and stayed with their grandmother, who took care of them till Ya-Wen returned to Taipei to continue secondary school.

In 1986, she attended the department of chemistry at National Taiwan University and obtained her bachelor of science degree in 1990. She then worked with Dr. T.-M. Su, the first person to teach her the *ab initio* theory in quantum chemistry. In 1992, she was admitted to the department of chemistry at the University of Florida. In 1993, she joined the group led by Dr. M. C. Zerner from the Quantum Theory Project, and later worked on a new semiempirical molecular orbital method for her Ph.D. dissertation.

For the first time in her life she left home to study in a foreign country. There were inevitable obstacles in her new life, but luckily she made her way through them with lots of help from friends around her. The Quantum Theory Project is a multinational group, and Ya-Wen therefore had the opportunity to meet people from different parts of the world, to learn more about cultural diversity, mutual understanding, and tolerance. In 1996 she met Mr. Magnus Hedström, an exchange student from Sweden. Mr. Hedström, who later became Dr. Hedström, gave her continuous encouragement and care. Finally in 1998, she married him, and they started their own family.

Aside from acdemic knowledge, Ya-Wen has learned many things during her stay in Florida, which would not have been possible if she had not gone abroad. There is a Chinese saying: “Learn from travelling ten thousand miles rather than from reading ten thousand books,” which well describes her experiences in the United States.

Before long, Ya-Wen and Magnus are moving to Europe, where she will continue with her ever-learning life.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Michael C. Zerner, Chair
Distinguished Professor of
Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

N. Yngve Öhrn
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John R. Sabin
Professor of Physics

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Philip J. Brucat
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Nigel Richards

Nigel G. J. Richards
Associate Professor of Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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Dean, Graduate School